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JOURNAL

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THE CHEMICAL SOCIETY.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

I.—*On the Estimation of Starch.*

By C. O'Sullivan.

Although the correct estimation of starch is a matter of much importance, the methods hitherto employed to effect that object are wanting in definiteness and precision, and even the best of them yield unsatisfactory results. The literature of the subject is too well known to necessitate reference here to the individual methods, and experimenters who have had many starch estimations to make are well acquainted with some of their defects. For the past eight or ten years I have employed a method of estimating starch in the cereals, and in malted grain—a method, no doubt, also applicable to other starch-containing substances—which yields, as I believe I can show, trustworthy results.

This method is based, amongst other things, on the correct estimation of maltose and dextrin: unfortunately I have hitherto been unable to satisfy myself that I have these bodies in my hands in a state of absolute purity, and, consequently, I have been unable to determine those factors upon which their accurate estimation depends to my perfect satisfaction: hence I have delayed drawing attention to the method. As, however, the required factors of maltose are established with sufficient exactness, and those I have determined for dextrin may be looked upon as being reasonably accurate, and, as I do not see my way in the immediate future to do more for dextrin than I have done, I may be permitted to describe the method as it stands, leaving any corrections it may require to the future.

The mode of operation is applicable to all the cereals, raw as well as malted, and may be briefly described as follows:—

A fair sample of the grain is taken, and of this 5·1 grams are weighed roughly and ground fine in a coffee-mill kept clean for the purpose. Of the finely-ground flour 5 grams, or thereabouts, accurately weighed, are introduced into a wide-necked flask capable of holding 100 to 120 c.c. The flour is just saturated with alcohol, sp. gr. 0·82, and then 20 to 25 c.c. ether added. The flask is corked and put aside for a few hours, the deposit being shaken occasionally. The clear ethereal solution is decanted through a filter and the residue washed by decantation with three or four fresh quantities of ether, the washings being passed through the filter. To the residue 80 to 90 c.c. alcohol, sp. gr. 0·90, are added, and the mixture kept at 35—38° for a few hours with occasional shaking. The alcoholic solution when clear is decanted through the filter used in filtering the ether solution, and the residue washed a few times by decantation with alcohol of the strength and at the temperature indicated. The residue in the flask, and any little that may have been decanted on to the filter, is then washed with water into a beaker capable of holding half a litre, and the beaker nearly filled with water. In about 24 hours the supernatant liquid becomes clear, when it can be gradually decanted through a filter. The solution filters bright, but in the case of barley and oats, exceedingly slowly at times; the malted grains, as well as wheat, rye, maize, and rice, yield solutions requiring no excessive time to filter. The residue is repeatedly washed with water at 35—38°, but even this, as we shall see, does not completely free barley and oats from α-amylan, which dissolves with the greatest difficulty at this temperature. The residue is then transferred to a 100 c.c. beaker, and the portion adhering to the filter washed by opening the filter-paper on a glass plate and removing every particle by means of a camel's hair brush, cut short, and a fine-spouted wash-bottle. When the transference is completed, the beaker, which should not now contain more than 40 to 45 c.c. of liquid, is boiled for a few minutes in the water-bath, care being taken to stir well when the starch is gelatinising to prevent "balling" or unequal gelatinisation. After this the beaker, still in the bath, is cooled to 62—63°, and 0·025 to 0·035 gram diastase,* dissolved in a few c.c. water, added. A trace of the

* The diastase employed is prepared as follows:—2 or 3 kilos. of finely ground pale barley malt are taken, sufficient water added to completely saturate it, and, when saturated, to slightly cover it. When this mixture has stood three or four hours as much of the solution as possible is pressed out by means of a filter-press. If the liquid is not bright it must be filtered. To the clear bright solution, alcohol sp. gr. 0·83 is added as long as a flocculent precipitate forms, the addition of the alcohol being discontinued as soon as the supernatant liquid becomes opalescent or milky.

solution ceases in a short time to give a blue colour with iodine, the starch being completely decomposed and dissolved, yet it is as well to continue the digestion at 62—63° for an hour, as the solution, as a rule, filters better. At the end of that time the contents of the beaker are boiled for eight or ten minutes, thrown on to a filter, and the filtrate received in a 100 c.c. measuring flask. The residue is carefully washed with small quantities of boiling water at a time. When the flask is nearly full, its contents are cooled down to 15·5° and made up to 100 c.c. with water at that temperature. If care be not taken to put on only small portions of water at a time during the washing, the filtrate may exceed 100 c.c. before the residue is perfectly free from soluble matter; in this case the solution must be evaporated to less than 100 c.c., and then made up to that bulk after cooling to 15·5°.

Treatment with ether frees the grain from fat, &c.; alcohol of 0·90 removes the sugars, the albuminoïds other than caseïn, &c.: and water at 35—38° is intended to dissolve the amylans, &c.; whilst the diastase is made to act on the residue at the temperature and under the conditions that it dissolves starch. The 100 c.c. solution contains, therefore, the products of the transformation or decomposition of that body. As we now know that dextrin and maltose are the only products of the action of diastase on starch, we have simply to estimate these bodies, and the quantity of starch is easily calculated.

It must, however, be proved:—

1stly. That the solvents employed before the diastase solution are without action on starch.

2ndly. That the insoluble residue is free from starch, and

3rdly. That the solution with diastase contains no optically active or reducing bodies other than the products of the decomposition of starch, or, if it does, that they are such as can be eliminated and allowed for.

1stly. The *purified* starches of the cereals, raw as well as malted, when treated with ether, alcohol, and water, are unacted upon. This would appear to be sufficient evidence that the solvents are without action on the starches; but it is not, as the purified starches are only those portions of the starch of the grains that resist the solvents employed in the process of purification. It is necessary in each case to prove that the different solutions obtained from the grain before treatment with diastase solution are free from soluble starch, dextrin,

The precipitate is washed with alcohol, 0·86—0·88, dehydrated with absolute alcohol, pressed between cloth to free it as much as possible from that liquid, and dried *in vacuo* over sulphuric acid until the weight becomes constant. Prepared in this way the substance is a white, friable, easily soluble powder, retaining its activity for a considerable time. The preparation usually sold as diastase is useless for this work.

and maltose. In working with malted grain, the alcoholic extracts contain maltose, amongst the other sugars, but dextrin is not present either in the alcoholic or aqueous extracts: hence, in these cases, I am forced to consider that the maltose is a result of the malting process and not derived from the starch by the treatment with the solvents. The alcoholic extracts of the raw grains do not contain maltose with the other sugars, and, in working with grain of *average ripeness* (I may state it is only such I have at present under consideration), the aqueous solution contains neither soluble starch nor either of its decomposition-products. It would take far too much space to describe here how these things have been proved, but the processes will form part of the methods for determining the other constituents of the cereals to be recorded in due time.

2ndly. The residue insoluble in diastase solution is easily proved to be free from starch by the iodine test.

3rdly. The following analyses of the 100 c.c. solutions from the cereals will enable us to arrive at satisfactory conclusions as to the bodies contained therein:—

Barley may be taken first. This grain is easily freed from fat, certain sugars and albuminoïds, other matters, and some of its ash constituents, by successive treatment with ether, dilute alcohol, and water; but it is impossible to wash out all the α-amylan without continuing the action of the solvent so long as to incur, even with the use of salicylic acid, the loss of starch by fermentation. Some amylan, as we shall see from an example, is therefore found in the 100 c.c. solution.

5 grams of barley-flour, treated as above, and acted upon with 0·03 gram diastase, gave 100 c.c. solution at 15·5°, having a sp. gr. = 1·01003 = 2·539 grams of solid matter, taking 1·00395 as the sp. gr. of a solution containing in 100 c.c. at 15·5° 1 gram of starch-products. 9·178 grams of this solution reduced 0·241 gram cupric oxide,* and a layer of it, 200 mm. in length, gave a deviation with a Soleil-Ventzke-Scheibler saccharimeter equal to 21·1 divisions. From these data we have:

$$0{\cdot}241 \times 0{\cdot}7256 \text{ (K of maltose } 62{\cdot}5) = 0{\cdot}1748 \text{ gram.}$$

maltose in 9·178 grams solution.

* Soxhlet (*J. pr. Chem.* [2], **21**, 227) has shown that the amount of cupric oxide reduced by a reducing body varies within certain limits; this is fairly obvious to any one who has had much to do with such matters; but it is equally clear that if the conditions of dilution, &c., at which the reducing and reducible solutions are brought together are kept constant, or even nearly so, and the process as described by me (*Chem. Soc. J.*, **25**, 581) adhered to, the cuprous oxide precipitated is a constant quantity.

100 c.c. solution = 101·003 grams; hence
9·178 : 101·003 : : 0·1748 : x maltose in the 100 c.c.
x = 1·923.

The optical activity of maltose may, for the concentrations we shall have to deal with, be taken as $\alpha_j = 154°$, ($\alpha_D = +139°$), and that of dextrin $[\alpha]_j = +222°$ ($\alpha_D = +200·4°$). With these values, 1 gram of maltose in 100 c.c. solution gives a deviation in a 200 mm. tube with the instrument above mentioned = 8·02 divisions, and 1 gram of dextrin in 100 c.c. in the same length of tube 11·56 divisions. Then—

1·923 × 8·02 = 15·422 the activity of the maltose.
21·1 − 15·422 = 5·678 „ „ dextrin.
and 5·678 ÷ 11·56 = 0·491 the dextrin in the 100 c.c. solution.

We have then in the 100 c.c.:—

Maltose	= 1·923	grams
Dextrin	= 0·491	„
Diastase	= 0·030	„
Total	2·444	„
Against	2·539	„ as represented by the sp. gr.
Leaving	0·095	„ matter unaccounted for.

To account for this, 75 c.c. of the solution were taken, evaporated to 30 c.c., cooled, and 60 c.c. alcohol, 0·84, added; no precipitate was produced, but the solution became opalescent. A few drops of hydrochloric acid were added with stirring; in a few seconds the liquid "broke" and a flocculent precipitate separated. This was allowed to subside, and the clear supernatant liquid was decanted off; it was then washed with 0·86 alcohol, dehydrated with strong alcohol, and collected on a tared filter. The body, dried over sulphuric acid *in vacuo* and in dry air at 100°, was perfectly white and friable, and proved, on examination, to be α-amylan. It weighed 0·062 gram.

We have, therefore, in the 100 c.c. solution—

Maltose	= 1·923	grams.
Dextrin	= 0·491	„
Diastase	= 0·030	„
α-Amylan = 0·062 + $\frac{0·062}{3}$	= 0·083	„
Total	2·527	„
Against	2·539	„
Leaving for error of manipulation	0·012	„

or less than half a per cent. on the total matter in solution: this must be considered satisfactory. The maltose and dextrin only are derived from the starch, the latter without increase in weight, the former with an increase of 5·5 per cent., *i.e.*, 1 part of starch yields 1·055 parts maltose: hence—

$$1{\cdot}055 : 1{\cdot}923 :: 1 : x \text{ starch} = \text{maltose.}$$
$$x = 1{\cdot}822 \text{ grams starch.}$$

Then	1·822	„	as maltose.
	0·491	„	„ dextrin.
Total	2·313	„	from the 5 grams barley.

This is 46·26 per cent. A second experiment with the same barley gave 46·38 per cent.

The α-amylan should be taken into the calculation if absolute accuracy be desired, but, as by allowing for it in the last determination, taking its optical activity to be $[\alpha]_j = -25°$, and its cupric oxide reducing power = 0, the starch comes out 46·44 per cent. against 46·26, it is obvious that the amylan was hardly worth the trouble of separating, and indeed when it is shown, by the difference between the total solids calculated from the sp. gr. and the sum of the dextrin, maltose, and diastase, to be so low as it is in this case, it may be fairly neglected.

In dealing with barley-malt this difficulty is not met with, because, as I have already stated (*Jour. Chem. Soc.*, **41**, 24), that material does not contain α-amylan. This substance yielded the following results:—

5 grams of barley-malt were treated as described, 0·030 gram of diastase being employed. The 100 c.c. solution obtained had a sp. gr. = 1·00829 = 2·099 grams solid matter. In a 200 mm. tube its optical activity was found to be +18·3 divisions (Sol. Ven. Sch.), whilst 10·493 grams of it reduced 0·233 gram cupric oxide. These data, calculated as in the previous case, show the 100 c.c. to contain:—

Maltose =	1·623	grams.	
Dextrin =	0·457	„	
Diastase =	0·030	„	
Total	2·110	„	
Against	2·099	„	calculated from sp. gr.
Difference	0·011	„	

This difference, amounting to only 0·5 per cent. on total matter, shows the accuracy of the dextrin and maltose determinations, and that we have no disturbing body to deal with.

1·623 grams maltose	=	1·538 grams starch and	
0·457 „ dextrin	=	0·457 „	„
Total		1·995 „	„

Or 39·90 per cent. on the malt.

Where it is known, in cases like this, that the solution contains nothing but starch products, the dextrin and maltose can be calculated by the equation—

$$8{\cdot}02x + 11{\cdot}56\ (s - x) = \alpha$$

in which x = maltose, s = dextrin and maltose (total solids — diastase), and α = the divisions (Sol. Ven. Sch.) observed, a 200 mm. tube being employed. Substituting for s and α the figures obtained in the last determination, we have—

$$x = 1{\cdot}581$$
$$\text{and } s - x = 0{\cdot}488$$
$$\text{Total } 2{\cdot}069$$

From these figures the total starch comes to 1·986 grams, being 39·72 per cent. against 39·90 by the combined cupric oxide and optical observations. This, notwithstanding, unless in cases where there is a certainty of the absence of all bodies other than dextrin and maltose, it is obviously more satisfactory to employ the combined observation method.

The results yielded by the chief cereals may be briefly stated as follows :—

Wheat :—6·009 grams white wheat, treated as described, gave, with 0·035 gram diastase, 100 c.c. solution, sp. gr. = 1·01394; in a 200 mm. its optical activity was 29·5 divisions; and 9·275 grams of it reduced 0·386 gram CuO. These data, worked out, show the solution to contain :—

Maltose.....	=	3·061 grams.	
Dextrin	=	0·428 „	
Diastase	=	0·035 „	
Total.....		3·524 „	
Solids indicated by sp. gr.	=	3·529 „	
Difference.....		0·005 „	
3·061 grams maltose	=	2·901 grams starch.	
0·428 „ dextrin	=	0·428 „	„
Total....		3·329 „	„

Or 55·40 per cent.

In a second experiment with the same sample, 4·94 grams wheat with 0·030 gram diastase gave 100 c.c. solution, sp. gr. = 1·01121, the optical activity being 24·6 divisions in a 200 mm. tube and 6·947 grams reducing 0·208 CuO. These data lead to—

Maltose.....	=	2·196 grams.
Dextrin.....	=	0·605 „
Diastase	=	0·030 „
Total.....		2·831 „
Solids indicated by sp. gr.	=	2·838 „
Difference.....		0·007 „

The starch-products are equal to 2·686 grams starch or 54·37 per cent., against 55·40 per cent. in the first experiment.

With wheat-malt the results are of a like character; the dextrin, maltose, and diastase together come out from 0·5 to 1·0 per cent. less than the solids, as indicated by the sp. gr. of the 100 c.c. solution. The malt of the above wheat gave—

1st Exp. 43·26 per cent. starch.
2nd „ 43·53 „ „

These numbers are sufficiently in accord to satisfy me that the method can be relied on, and that its errors may be neglected, at least for the present.

Rye behaves like wheat if the washings are carefully performed and the grain moderately *ripe;* the maltose, dextrin, and diastase differing but slightly from the solids calculated from the specific gravity, showing that there is no disturbing constituent to interfere with the accuracy of the determinations. Ripe rye yielded from 44 to 46 per cent. starch.

Rice and maize also, when treated as directed, yield a pure dextrin-maltose solution: the rices I have examined contained from 75 to 77 per cent. starch, and the samples of maize (yellow) from 54 to 58 per cent.

Oats do not yield a pure dextrin-maltose solution, even though the washings are most carefully done; the solids as indicated by the sp. gr. are always from 2 to 3 per cent. greater than the sum of the dextrin, maltose, and diastase. The body causing this difference behaves like α-amylan, but I have not yet proved it to be that body. The mean results however cannot be more than 0·5 per cent. removed from the truth. Ripe white oats were found to contain from 35 to 38 per cent. starch.

In order to show more fully how far the method of determination

is to be relied upon, I submitted a known quantity of purified starch to the processes. The results obtained are, no doubt, only of value when it is proved that the solvents employed before the diastase solution do not dissolve any starch; this, as I have before stated, as far as ripe grain is concerned, may be taken as proved.

4 grams pure starch containing 10·64 per cent. water, treated with ether, dilute alcohol, water, and diastase solution containing 0·030 gram diastase, gave 100 c.c. solution, sp. gr. 1·01459 = 3·694 grams dry solids. 6·439 grams of this solution reduced 0·249 gram CuO, and in a 200 mm. tube its optical activity was found to be 32·2 divisions. These numbers calculated as usual lead to—

Maltose	= 2·848	grams in	the 100 c.c.
Dextrin	= 0·809	,,	,,
Add diastase	= 0·030	,,	,,
Total ..	3·687	,,	,,
Against	3·694	,,	,,

calculated from the specific gravity.

The maltose is equal to	2·700	grams starch and
The dextrin ,,	0·809	,,
Total	3·509	,,

Or 87·72 per cent. dry starch in the sample.

As stated, this sample contains 10·64 per cent. water, and, therefore, 89·36 per cent. dry starch, or 1·64 per cent. more than found; this covers undissolved matter, impurity, loss, and error of manipulation.

6·122 grams of the same starch treated with 0·048 gram diastase yielded 100 c.c. solution of sp. gr. 1·02227 = 5·639 grams solid matter. The optical activity in a 200 mm. tube was 55·6 divisions, and 4·403 grams of the solution reduced 0·157 gram cupric oxide. These numbers work out:—

Maltose	= 2·647	grams in	the 100 c.c.
Dextrin	= 2·974	,,	,,
Diastase	= 0·048	,,	,,
Total.....	5·669	,,	,,
Solids from sp. gr.	= 5·639	,,	,,
Difference	0·030	,,	,,
The maltose	= 2·509	grams starch.	
The dextrin	= 2·974	,,	
Total	5·483	,,	

or 89·54 per cent. dry starch against 89·36 per cent., the known quantity.

These experiments convey a fair idea of the extent to which the method is to be relied upon, and further show that the accuracy is the same whether the dextrin be high, as in the last experiment, or low, as in the previous one.

I need hardly state that the optical observations can be made with any of the sodium flame polarimeters, or with a Soleil-Duboscq, but, then the factors proper to those instruments must be substituted for the figures employed in the above calculations. As an example we may take the analysis of the last 100 c.c. solution. With a Laurent, in a 200 mm. tube, the deviation was 19·25°. The optical activity of maltose is $[\alpha]_D = + 139°$, and of dextrin, $[\alpha]_D = 200·4°$; hence, 1 gram maltose in 100 c.c. solution exhibits an activity in a 200 mm. tube with the sodium flame of 2·78°, and a solution of dextrin of the same strength an activity of 4·008°. The amount of cupric oxide reduced showed the maltose, in the experiment under consideration, to be 2·647 gram in the 100 c.c. $2·647 \times 2·78 = 7·359$, the degrees due to maltose; then $19·25° - 7·359 = 11·891$, the degrees due to dextrin; and $11·891 \div 4·008 = 2·966$, the grams of dextrin in 100 c.c. solution. The observation with the Soleil-Ventzke-Scheibler gave 2·974 grams.

In conclusion, I may mention that the experiments quoted here have been selected from many made by Messrs. J. O'Sullivan, F. W. Tompson, and myself, and that they are chosen to show rather the general tendency of the results than the accuracy with which the determinations can be made. My experience with the method is, that the difference in results obtained by any two observers need not exceed, at the outside, 0·5 per cent. of total starch. We have also the security in working with this method that starch and starch only is being dealt with.

II.—*On the Oxidation of Phosphorus at a Low Temperature, and the Alleged Decomposition of Phosphorous Anhydride by Sunlight.*

By R. Cowper and Vivian B. Lewes, Royal Naval College.

In a paper read before the Southport meeting of the British Association, by the Rev. A. Irving, on the "Action of Sunlight on Phosphorous Anhydride," the author states that phosphorous anhydride, prepared by passing a slow stream of dry air over molten phosphorus,

decomposes when exposed to sunlight into amorphous phosphorus and phosphoric anhydride, and he mentions that this action has also been noticed in Wislicenus's edition of Strecker's Chemistry.

Wishing to verify these statements, we repeated the experiment described by Mr. Irving, and slowly passed well-dried air over molten phosphorus contained in the bend of a **V**-tube, one arm of which was of considerable length and drawn out at intervals of 6 inches, so as to form three small chambers. The air, dried by passing through two chloride of calcium tubes and a wash-bottle of sulphuric acid, was passed into the short arm of the **V**-tube and over the phosphorus, which was just kept above its melting point in a water-bath, the products of the action being deposited in the chambers of the long arm of the **V**.

The deposit close to the phosphorus was reddish-brown, and in the first chamber was slightly coloured, but in the two upper portions of the tube was perfectly white. These two portions were sealed off at the strangulations, and one was placed in direct sunlight, whilst the other was kept in the dark. The tube exposed to sunlight soon lost its pure white colour, and after a few hours changed to light brown, whilst the tube which had been kept in the dark remained perfectly white; but on examining it through a lens, the surface of the glass above the deposit was seen to be spangled with minute and very brilliant crystals, and on opening the tube and shaking out the contents, the latter spontaneously inflamed.

The presence of the crystals in the tube at once suggested that the deposit was not pure phosphorous anhydride, but a mixture containing finely divided crystalline phosphorus, and as this would fully explain the phenomena described by Mr. Irving, we determined if possible to clear up this point.

The previous experiment was repeated, the temperature of the water-bath being from 52° to 56° C., and the air being passed at such a rate that the phosphorus just faintly glowed at the point with which the air first came in contact. The tubes containing the deposit were sealed off as before, and the centre tube of the three was taken for analysis.

The tube having been weighed had one end carefully cut off, and was immediately filled with distilled water, and the contents washed out upon a filter; the tube after careful rinsing being again dried and weighed.

The residue on the filter-paper, after careful washing, was readily shown to be phosphorus, as on drying the paper on a warm dish the small crystals caught fire and burnt away, charring the paper. The filtrate was then made up to 50 c.c., and the phosphorous anhydride was determined in 25 c.c. by its reducing action on mercuric chloride,

the remaining 25 c.c. being evaporated to a syrup with strong nitric acid to convert any phosphites into phosphates, and the total phosphate was determined as magnesium pyrophosphate, all the usual precautions being observed. The numbers so obtained give the quantities of phosphorous and phosphoric anhydrides, and the amount of phosphorus is calculated from the difference between these and the weight of the contents of the tube.

Weight of deposit in tube ..	0·029

Consisting of—

Phosphoric anhydride	0·0206	or 71·0	per cent.
Phosphorous „	0·0028	„ 9·6	„
Phosphorus (by diff.)	0·0056	„ 19·3	„

showing that instead of being pure phosphorous anhydride, it was practically a mixture of phosphoric anhydride and phosphorus with a small quantity of phosphorous anhydride.

Another series of tubes was then prepared, the temperature of the water-bath heating the phosphorus being allowed to reach 62°, whilst the rate at which the air was allowed to pass continued about the same; and the contents of the centre tube were analysed as before, giving—

Phosphoric anhydride	0·0572	or 70·1	per cent.
Phosphorous „	0·0017	„ 3·2	„
Phosphorus (by diff.)	0·0141	„ 26·6	„
Weight of deposit.....	0·0530		

In a third experiment the phosphorus was melted by a small naked Bunsen flame, as in Mr. Irving's original experiment, and the results obtained on analysis were:—

Phosphoric anhydride	0·0219	or 78·2	per cent.
Phosphorous „	0·0013	„ 4·7	„
Phosphorus (by diff.)	0·0048	„ 17·0	„
Weight of deposit.....	0·0280		

Another experiment was then made in which the products of the action, after passing through one depositing tube, were made to pass through a small wash-bottle containing bisulphide of carbon, the escape of which was prevented by an upright Liebig's condenser connected with it.

After the products had passed through it for some time, the bisulphide of carbon was allowed to evaporate spontaneously on blotting-

paper, leaving enough phosphorus behind to give dense fumes, but not enough to ignite the paper.

From these experiments it is evident that Mr. Irving's so-called phosphorous anhydride is a mixture containing minute crystals of phosphorus, which are rendered amorphous when exposed to sunlight, and it seems highly probable that the spontaneous inflammability claimed for phosphorous anhydride is due to the same cause.

University of

III.—*On the Constitution of the Fulminates.*

By Edward Divers, M.D., and M. Kawakita, M.E.

The authors' attention has been drawn to the chemistry of the fulminates in consequence of Steiner's recommendation of mercury fulminate as a source of pure hydroxyammonium chloride, which he has shown to be a product of its decomposition, without apparently being aware that the same interesting fact had but a short time before been discovered by Carstanjen and Ehrenberg. (*J. pr. Chem.* [2], **25**, 232—248.) As one of us was in want of hydroxylammonium chloride free from ammonia, we followed Steiner's directions, not only with the attainment of our object, but with a discovery complementary to that of hydroxylamine among the products of the decomposition, which has led us to some further observations, to be followed we hope by more; and has suggested a theory of the constitution of fulminic acid, which will be treated of by one of us in the latter part of this communication.*

Mercury Fulminate as a Source of Hydroxylamine free from Ammonia.

To Carstanjen and Ehrenberg belongs the discovery of the production of hydroxylamine from mercury fulminate, but we shall refer at first more fully to Steiner's paper, because it was that which suggested our own work.

Steiner was induced, he states, to make his recent experiments by

* We are unable, here in Japan, to consult many original papers. Our literature of this subject has been the admirable history of the fulminates in *Watts's Dictionary*; Armstrong and Groves's edition of *Miller's Organic Chemistry*; Roscoe and Schorlemmer's *Chemistry*; *The Journal of the Chemical Society* (Abstracts); and recent volumes of the *Berichte*.

a consideration of the researches of Victor Meyer on nitroso-compounds, which have shown that the production of hydroxylamine by the action of hydrochloric acid is a test for isonitrosyl, or N.OH derivatives.

By the use of this acid he has obtained the nitrogen of the fulminate in the form of hydroxylamine, and failed to find anything else whatever, even losing sight of the carbon. Above all, no ammonia is found; and he therefore recommends the reaction between hydrochloric acid and mercury fulminate for the preparation of pure hydroxyammonium chloride.

His process consists in mixing the moist fulminate with fuming hydrochloric acid, cooling the mixture at first, then heating and evaporating to a small volume, diluting with water, precipitating mercury with hydrogen sulphide, filtering, and evaporating to crystallisation, or even to dryness. It has proved quite successful in our hands, and we consider that no method of preparing hydroxylamine previously in use can compare with it. There being, it is seen, scarcely any manipulation of the fulminate necessary, danger hardly attends the process in careful hands.

Production of Hydrocyanic Acid.

Steiner found no trace of bye-products in his experiments; but in ours we at once detected hydrocyanic acid by its smell, in spite of the hydrochloric acid fumes. The formation of this body seeming to us to affect seriously his views of the simple constitution of fulminic acid, we proceeded to determine the extent to which it went.

A strongly fuming solution of hydrochloric acid was poured through a stoppered funnel on to about 4 grams of wet mercury fulminate contained in a retort, connected with a tube-receiver holding potassium hydroxide solution. At first the retort was cooled, then heated. Afterwards, through the funnel, water was run in, and distillation carried on for some time. Lastly, the cyanide in the receiver was determined volumetrically by Liebig's method, and the mercury in solution in the retort-residue determined as sulphide. In the retort were some mercury globules, mixed up originally with the crude mercury fulminate, and a little calomel:* these were filtered off before precipitating the mercury sulphide. Calculating the mercury into fulminate, we found that the latter had yielded not more than 0·15 per cent. of hydrocyanic acid, which is equal to 0·5

* The presence of metallic mercury in a preparation of fulminate is due to the action having been too much checked, in accordance with the caution usually recommended. The action should be allowed a free course, and if danger is apprehended, suitable precautions taken against it.

part of this in 100 parts of fulminic acid. There was certainly one slight error in the analysis, due to the volatilisation of mercuric chloride during distillation, and the formation of a little calomel in the latter part of this operation; but taken with the results here and afterwards obtained, this was a fact of little importance, and we did not attempt more accurate experiments.

What we did next was to purify some fulminate by recrystallisation, and then repeat our experiments qualitatively. Again we smelt hydrocyanic acid, and by exposing a film of potash-solution to the very acid vapours for a time, too short to let it get neutralised, we obtained in it the Prussian-blue reaction in a well marked way. We proceeded sometimes by adding the fulminate to the acid, and sometimes by pouring this over the fulminate, and got the same result each way. We also succeeded with fulminate prepared free from metallic mercury and not recrystallised, but proved by quantitative analysis to be pure.

After we had concluded this part of our work, we came across Carstanjen and Ehrenberg's paper (Abstr. in *Berichte*), and found that they too had noticed a little hydrocyanic acid. "According to Ittner, aqueous hydrochloric acid produces a large quantity of hydrocyanic acid" (*Watts's Dictionary*). Hitherto, we had followed Steiner and used moist fulminate and concentrated hydrochloric acid. We now tried dilute acid, and got much hydrocyanic acid. Next, to fuming hydrochloric acid we added dry fulminate,* and in this form of the experiment we at last obtained not a trace of hydrocyanic acid.

Yield of Hydroxylamine.

Steiner has not determined the quantity of hydroxylamine yielded by mercury fulminate. But from his constitutional formula for fulminic acid and from his experiments, the whole of the nitrogen would be expected to form this substance. We made one experiment with no great claim to accuracy, and found that this was the case, and for the time we were satisfied. But then we saw that Carstanjen and Ehrenberg in their experiments got only 16½ grams of hydroxyammonium chloride from 50 grams of fulminate, whereas all the nitrogen would have given 24·44 grams, or half as much again. The following experiment was therefore next made by us. Having prepared some fulminate free from metallic mercury without recrystallising, which is an unsatisfactory operation, we washed and dried it, and treated

* The addition of dry fulminate to concentrated hydrochloric acid may possibly be a dangerous operation, but it was made by us without any evidence of this being the case. The fulminate fell to the bottom of the acid, and readily dissolved on shaking.

2·351 grams of it with excess of fuming hydrochloric acid and, after separation of the mercury as sulphide, made up the filtered solution to 250 c.c. Of this, 1 part kept slightly alkaline during the operation, was titrated with iodine, and gave the theoretical yield, that is, 48·84 instead of 48·87 per cent. Another part was evaporated to dryness in a platinum capsule, and the white residue weighed. The result was equivalent to 47·44 per cent. This residue was then dissolved in water, and titrated with iodine, giving then 47·21 per cent. These numbers serve to show that the whole of the nitrogen, and not merely two-thirds of it, is converted into hydroxyammonium chloride by fuming hydrochloric acid. Besides hydroxyammonium chloride, Carstanjen and Ehrenberg got only a little hydrocyanic acid, and therefore, with this exception, have given no account of what became of the other third of the nitrogen.

The Carbon of Mercury Fulminate becomes Formic Acid.

Some mercury fulminate was distilled in a retort with fuming hydrochloric down to a very small volume, a little water having been placed in the receiver. The distillate contained hydrochloric acid, a trace of hydrocyanic acid, a very little mercuric chloride, and much formic acid. No glyoxylic acid, or indeed anything else, was found. The retort residue deposited calomel during the distillation.

In the identification of formic acid we got the two mercury reactions, the silver reaction and the iron reaction, all in a well-marked way. We neutralised the remainder of the distillate with calcite. The clear solution gave a precipitate with absolute alcohol. The mother-liquor still contained some formate, soluble in the diluted alcohol. The precipitate was washed with absolute alcohol, in which it appeared almost insoluble, until free from chloride. It was then examined and found to be very soluble in water, to give the reactions of a formate, to turn very slightly grey only, for a moment, when heated, and not to char, and to yield, on ignition, lime equal to 42·94 per cent., calculation for formate giving 43·08 per cent.

In the fact that, although formic acid is not affected by mercuric chloride in solution in concentrated hydrochloric acid, it is quickly oxidised by it when the acid is very dilute, will be found, we think, the cause of formic acid having escaped the attention of other chemists. Steiner's formula for fulminic acid would naturally suggest the production of formic acid from it.

Behaviour of Hydroxylamine to Litmus.

Hydroxyammonium chloride, though without acid taste, reacts markedly with litmus, and when a weighed quantity of it is titrated

with potassium hydroxide, it takes almost exactly the equivalent of the hydrochloric acid it should contain, to turn the litmus blue. In one trial 0·524 gram of hydroxyammonium chloride gave 0·280 gram hydrochloric acid, or 1·8 per cent. too much, showing the salt to have been slightly acid.

We believe we are here stating what has not yet been observed by others. But our reference library is limited. It is many years since one of us read and took notes of Lossen's papers, and those notes do not now help us. Hydroxylamine is said to have a strong alkaline reaction (Roscoe and Schorlemmer); but has it ever, before the recent researches on mercury fulminate, been obtained quite free from ammonia?

Yield of Formic Acid.

The presence of so much hydrochloric acid, of mercury chloride, and of hydroxylamine, which, like formic acid itself, reduces mercury salts, greatly limits the means of estimating formic acid. We have employed the following simple method with fair success:—

A weighed quantity of mercuric fulminate is added to excess but measured quantity of fuming hydrochloric acid contained in a retort connected with a receiver holding water. After heating for some time, the contents of the retort and receiver are mixed and diluted, and the mercury is precipitated by hydrogen sulphide. By warming and exposure to air in open vessels, the hydrogen sulphide is for the most part dissipated. The solution is then titrated with potassium hydroxide, as well as another quantity of hydrochloric acid equal to that used with the fulminate. As the mercury chloride is reconverted into hydrochloric acid by the hydrogen sulphide, and as the hydroxylamine does not neutralise to litmus the hydrochloric acid combined with it, there is an equal amount of hydrochloric acid free or available in the two solutions. Any excess of acid in the one which has received the fulminate will, therefore, be due to the formic acid generated from the fulminate.

By this method we have obtained 31·31 per cent. of formic acid, instead of 32·40 calculated, working on 2·6665 grams fulminate.

We are now therefore justified in writing

$$C_2H_2N_2O_2 + 4H_2O = 2CH_2O_2 + 2NH_3O,$$

as the change which mercury fulminate suffers under the influence of concentrated hydrochloric acid.

Analysis of Mercury Fulminate.

"The only fulminate of which a satisfactory analysis has been made is the silver salt" (*Watts's Dictionary*). In face of this state-

ment, it may be worth tabulating our analytical results in respect to the mercury salt.

Mercury fulminate, 2·351 grams, dissolved, as already described, in hydrochloric acid afterwards diluted, gave mercury sulphide, equal to 70·40 per cent. mercury. The same solution, after removal of mercury, titrated by iodine for hydroxylamine, gave nitrogen equal to 9·85 per cent., and, when evaporated, gave hydroxyammonium chloride equal to 9·55 per cent. A solution of 2·6665 grams fulminate in hydrochloric acid of known amount, after removal of mercury by hydrogen sulphide, gave, by titration with potassium hydroxide, formic acid, equal to 8·17 per cent. of carbon. Collecting and comparing with calculation from the formula, we get—

	Calc.	I.	II.	III.
Mercury	70·42	70·40	—	—
Nitrogen	9·86	9·85	9·55	—
Carbon	8·45	—	—	8·17
Oxygen	11·27	—	—	—
	100·00			

The carbon is a little low, but this is attributable to its loss as hydrocyanic acid, because the conditions of the carbon determination required the use of *moist* fulminate.

Mercury Fulminate does not yield Oxalate.

Not a trace of oxalic acid is produced by the decomposition of mercury fulminate by concentrated hydrochloric acid, by dilute hydrochloric acid, by sulphuric acid, or by hydrogen sulphide, according to our experience, which is in this respect, however, quite opposed to the statements made by other chemists, that oxalic acid is among the products of the decomposition of mercury fulminated by these reagents.

The discoverer of the fulminates, Howard, looked upon them as containing oxalate, and found mercurous oxalate as one of the products of the decomposition of the mercury salt by hydrochloric acid. Brugnatelli believed fulminating silver to be silver oxalate, and other chemists regarded the fulminates as double oxalates. Carstanjen and Ehrenberg state that mercurous oxalate is formed from the fulminate by the action of sulphuric acid (1 : 5). We have made repeated experiments on this point, and have never obtained any oxalic acid either in solution or in any precipitate. The precipitate with dilute hydrochloric acid is calomel; that with sulphuric acid is mercurous sulphate, as pointed out by Berthollet. We decomposed it thoroughly

both by hydrogen sulphide and by sodium carbonate solution, and found nothing but sulphate; at any rate it contains no oxalate. Carbonic acid is produced.

Theory of the Constitution of Fulminates.

By Edward Divers.

The knowledge that the fulminates contain two isonitrosyl radicals or their equivalent, and two formic carbons, greatly simplifies the question as to the constitution of fulminic acid, and divests the answer of much of its difficulty.

A theory of the constitution of the fulminates must, before it can be accepted, include an explanation of the formation of these bodies; of their capacity to yield cyanogen compounds, and to yield all their nitrogen as hydroxylamine, and all their carbon as formic acid; of their general if not entire disability to give dicarbon decomposition-products; of the difficulty in replacing more than half their silver or mercury by another metal; of their reactions with chlorine and bromine; and of their explosive character.

A notice of four of the formulæ which have been proposed will make apparent the extent to which they each fulfil these requirements of a theory of the subject. The four are—

Berzelius's, modernised	$Ag_2O,(AgN)_2,C_4N_2O_3$;
Kekulé's.....	$NC.CH_2(NO_2)$;
Armstrong's	HO.N:C:CH(NO);
Steiner's	HO.N:C:C:N.OH.

The first furnishes an explanation of the explosive character of the fulminates, representing the metal as combined with both nitrogen and oxygen. It also shows a difference in the relations of the two atoms of hydrogen, or of the metal in place of them.

The second also explains, but in a less satisfactory way, the fulminating character of these salts. It shows why cyanogen derivatives are so readily formed from them; and represents half the nitrogen as oxidised and able to become hydrogenised and produce hydroxylamine, just as nitroethane can. But it makes a nitroxyl radical to be introduced by nitrous acid, which, as Armstrong and Groves point out, it should not do. It entirely fails to account for the two kinds of acid properties the fulminates possess, and allows of only half the nitrogen becoming hydroxylamine.

The third formula explains the dual nature of the acidity, and also the formation of hydroxylamine and of cyanogen compounds. It is interesting as exhibiting the presence of isonitrosyl in fulminates, before this had been established by experiment. But it has become open to the objection, through the recent conclusions of Victor Meyer and his school, that nitrosyl does not get introduced into a CH_3 or CH_2-group; and probably its proposer would now reject it himself on that account.

The fourth formula is satisfactory as regards hydroxylamine and formic acid, but it does not make the cause of the explosive character apparent, nor the production of cyanogen compounds very probable, and, above all, it represents the two hydrogens as being of equal value. Besides this, it makes the hydrogen of isonitrosyl strongly basic, although this is not its character in other isonitrosyl compounds. We should expect, too, the formation of glyoxylic acid, but we do not find a trace of this body. The reaction would be—

$$\begin{matrix} C.N.OH \\ C.N.OH \end{matrix} + 3H_2O = \begin{matrix} CO.OH \\ COH \end{matrix} + 2H_2N.OH.$$

I shall now present what seems to me to be a satisfactory theory of all the facts bearing upon the constitution of the fulminates. It is that they are formed from (1) an alcohol residue in which the hydrogen has been replaced by metal, and which retains only the carbon and oxygen; and (2) a condensed hydroxylamine residue.

Hydroxylamine is now always formulated as an amine, $H_2N.OH$; but, so far as I know, between doing this and formulating it as an ammonium hydroxide, $H_3N(OH)_2$, there is little to enable us to decide. Its want of odour is perhaps in favour of the latter view. But it may quite probably have still another composition, to which I wish to call particular attention. It may consist, like ether, of two molecules condensed into one with loss of a molecule of water, thus :—

$$2H_2N.OH = (H_2N)_2O + H_2O.$$

That is, there is no known reason why $(H_2N)_2O$ should not be the composition of hydroxylamine, oxyammonia, or *amidogen oxide*, its derivatives being related sometimes to this condensed form, sometimes to its simple or alcoholic form of amidogen hydroxide. There is at least one piece of evidence of the existence of the condensed or oxide form, and that is the action of hydrochloric acid upon hydroxylamine. When solution of hydroxylamine is treated with a quantity of hydrochloric acid less than sufficient to saturate it, crystalline hemichloride of hydroxyammonium is obtained on evaporation (Lossen). Its constitution must be, it would seem, as shown in the equation :—

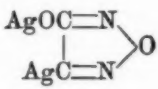
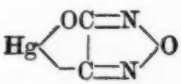
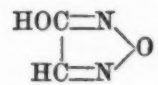
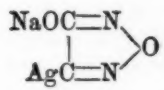
$$(H_2N)_2O + H_2O + HCl = \left.\begin{matrix}(HO)H_2N\\ ClH_2N\end{matrix}\right\} O,$$

and a second molecule of hydrochloric acid will convert it into ordinary hydroxyammonium chloride—

$$\left.\begin{matrix}(HO)H_2N\\ ClH_2N\end{matrix}\right\} O + HCl = 2ClH_3N(OH).$$

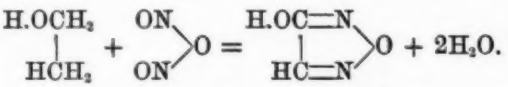
The absence of marked acid or alkaline reaction of hydroxylamine with litmus seems also to be a fact in favour of its oxide formula.

Coming now to the fulminates, their formulæ are in accordance with my description—

and these I proceed next to consider as to their sufficiency for expressing the facts.

First, as to the formation. Nothing could be more simple. The alcohol yields two-thirds of its hydrogen to the oxygen of the nitrogen-trioxide, and its carbons unite with nitrogen—

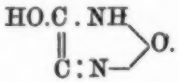


The fulminic acid here represented will either only be thus formed in the presence of mercury or silver nitrate, or it will be a transition body which would at once decompose but for the presence of the mercury or silver nitrate, with which it at once undergoes double decomposition, in virtue of being a cyanogen derivative, and just as the otherwise unstable hydrogen cyanide would do in similar circumstances. It is well known, on the authority of Liebig, that nitrogen trioxide passed into alcoholic solution of either mercury or silver nitrate, precipitates fulminate without evolution of gas.

Secondly, as to the character of the metallic or basic element of their constitution. The formation of fulminates under the operation of mercury or silver nitrate, and the displacement of only half these metals from their fulminates by the action of soluble chlorides, are facts in entire agreement with what we know of the cyanides of these metals. Hydrocyanic acid decomposes strongly acid solutions of mercury and silver, and potassium cyanide is decomposed even by the oxides of these metals, as every chemist knows, and their cyanides

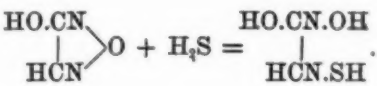
give stability to the unstable alkali cyanides when combined with them.

Thirdly, as to their explosive properties. To account for these, the presence together of the constitution of a cyanide and that of an oxygen salt seems fully sufficient. Berzelius's view of the matter resembles this explanation, allowance being made for the state of chemistry at the time he wrote. Indeed a formula may be given to fulminates, making out, as his does, that the metal is half united to nitrogen and half to oxygen, which has engaged my attention.

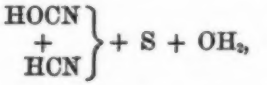


This formula is compatible with most of the facts; but that of the formation from alcohol is, as regards the transference required of the hydrogen from the carbon to the nitrogen, difficult to explain. Its relation to hydroxylamine is also not very simple.

Fourthly, as to the production of cyanogen compounds in their decompositions. This follows from the nitrogen being directly united to the carbon. The union with hydrogen sulphide (Steiner) may take place in this way—



This becomes in presence of water—



and then with a second molecule of hydrogen sulphide—

$$HOCN + H_2S = HSCN + H_2O,$$

besides

$$HOCN + H_2O = CO_2 + NH_3$$

and

$$HCN + S = HCNS.$$

When moist mercury fulminate is treated with hydrogen sulphide, some of the hydrocyanic acid always escapes at first.* Ammonia, carbon dioxide, thiocyanic acid, and sulphur, are all found (Steiner and others) in accordance with the above representation. Only Steiner gives oxalic acid as one of the ultimate products. How a reducing agent like hydrogen sulphide can produce oxalic acid is most

* For another mode of formation of hydrogen cyanide consult the paragraph on formic acid following.

difficult to conceive. Mr. Kawakita and I have not yet closely followed his experiments on the matter, but I confess that I think that there must be some mistake in them. The ordinary decomposition by hydrogen sulphide gives no oxalic acid.

Gladstone's formation of urea by ammonia and hydrogen sulphide follows from the preceding representation, in which cyanic acid appears, as this would of course give urea with the ammonia also present.

Fifthly, as to the formation of hydroxylamine and formic acid. To explain this we have the equation—

$$\begin{matrix} HOCN \\ | \\ HCN \end{matrix}\!\!>O + 2HCl + 4H_2O = \left\{\begin{matrix} HOCO \\ H \\ + \\ H \\ O \\ HCO \end{matrix}\right. + 2ClH_3NOH,$$

the $\equiv N_2O$ taking one molecule of water to become $2(=NOH)$, and the C_2 taking another to separate them (as when oxalic acid becomes formic and carbonic acids, and just for the same reason that they are only loosely held together, through all the ethane-hydrogen having been displaced). Each $=CN-$ takes a molecule of water to separate its elements to form on the one side carbonyl and on the other amidogen, as is usual with the cyanogen radical.

The production of formic acid and other monocarbon compounds only, is thus seen to be consistent with the dicarbon constitution derived from alcohol, while the formation of oxalic acid is not very improbable, provided there is a source of oxygen. Mr. Kawakita and I have, however, thrown great doubt on this formation in the decompositions in which it is stated by some chemists to occur, as will have been seen from our experiments. When mercuric fulminate is boiled with dilute sulphuric acid, there is an effective oxidising agent present in the mercuric oxide, which becomes mercurous sulphate, and here therefore are the conditions, it would seem, under which oxalic acid should appear. But Mr. Kawakita and I altogether fail to get it, and only formic and carbonic acids are obtained. Whether it is produced, but entirely decomposes in the hot sulphuric acid, we cannot determine, but I may mention that acid of 1 : 5 acts but slowly when boiling, and exceedingly slowly at only 100°; so that, without a temperature sufficient to cause the evolution of carbon dioxide, no change occurs. In our experiments, some were made in which 100° was maintained for a long time and not passed, and in these some fulminate remained undecomposed, but not a trace of oxalate was formed. The reaction for carbonic acid is as follows, in its first stage:—

$$\left.\begin{matrix} Hg''<^{OCN}_{CN}>O \\ + \\ Hg''<^{OCN}_{CN}>O \end{matrix}\right\} + H_2SO_4 + H_2O = \left\{\begin{matrix} ^{HCN}_{HOCN}>O \\ + \\ HO.OCN \\ \quad HCN>O \end{matrix}\right. + Hg'_2SO_4;$$

and then the fulminic acid shown in the upper line yields formic acid, and the lower (transition) acid yields formic acid and carbonic acid by further hydration.

Carbonic acid and hydrocyanic acid are also formed together under the influence of dilute hydrochloric acid. In this case only half the cyanogen of the fulminate undergoes hydration—the half combined with hydroxyl and apparently therefore less stable than the other:—

$$\begin{matrix} HOCN \\ | \\ HCN \end{matrix}>O + 2H_2O = \left\{\begin{matrix} (HO)_2CO + H_2NOH \\ \quad + HCN \end{matrix}\right.$$

Lastly, as to the action of bromine or chlorine. The primary reaction of bromine to form a body corresponding in composition with fulminic acid, but certainly not in constitution, admits now for the first time of ready explanation, without resorting to intra-molecular transposition:—

$$Hg<^{OCN}_{CN}> + 2Br_2 = HgBr_2 + \begin{matrix} OCN \\ Br_2CN \end{matrix}>O.$$

The product cannot on the present view retain its generally accepted name of dibromoacetonitril, its carbons being detached. Its conversion to bromopicrin and cyanogen bromide by excess of bromine in alkaline solution, is as intelligible as the formation of bromopicrin by hypobromite in other cases:—

$$Br_2 + OCN.O.Br_2CN = BrCN + Br_3CNO,$$

one atom of bromine replacing an atom of oxygen, and by thus leaving three-fourths of the combining power of the carbon to the nitrogen causing this to leave the other oxygen to the other nitrogen. Thus, we get cyanogen bromide. Then the oxygen displaced by bromine acts in the form of hypobromite as an oxidising agent on the NO, changing it to NO_2, the second atom of bromine combining with the carbon now only a quarter united to the nitrogen.

Mr. Kawakita and I intend to examine further the interesting body, $C_2N_2O_2Br_2$.

IV.—*Note on the Formation and on the Constitution of the Fulminates.*

By Henry E. Armstrong, F.R.S.

As the formula of the fulminates proposed by me is among those discussed by Dr. Divers in the foregoing communication, I may be allowed briefly to criticise his proposal and to state my present views on the subject.

The formula in question, (HO.N) : C : CH(NO) (which I should now prefer to write thus, (HO.N)C.H.NO) was first publicly mentioned in the course of some remarks I made at a meeting of the Society on April 1st, 1875, when Professor Hofmann read a paper "On the Action of Ammonia and Sulphuretted Hydrogen on the Fulminates," the work of one of his students, Mr. R. Steiner.

My reasons for dissenting from Kekulé's formula are sufficiently stated in *Miller's Elements of Chemistry*, vol. iii, 5th edition, p. 176.

In proposing an alternative formula, I was led to assume that half the nitrogen was present in the form of nitrosyl, NO, and the other half in the form of *hydroximide*,* N.OH, because I took for granted that the fulminates were the products of the direct action of *nitrous acid* upon *alcohol*, it being known from Victor Meyer's researches that both of these groups could be introduced through the agency of nitrous acid; the assumption that the fulminates were nitroso-derivatives also appeared to account for the formation of *nitro*trichloromethane on distilling them with bleaching powder, as it was known that certain nitroso-compounds were easily converted by oxidation into nitro-compounds.

But as Dr. Divers observes, Victor Meyer's more recent researches have shown that the radicle NO is not introducible into a CH_3 or CH_2 group by means of nitrous acid. My formula certainly requires modification on this account, the equation which I have given as expressing the primary reaction:

$$\begin{matrix} CH_3 \\ CH_2.OH \end{matrix} + \begin{matrix} NO.OH \\ NO.OH \end{matrix} = \begin{matrix} CH_2.NO \\ C(N.OH).OH \end{matrix} + \begin{matrix} OH_2 \\ OH_2 \end{matrix},$$

being thus far incompatible with our present state of knowledge as to the action of nitrous acid.

* Instead of terming N.OH derivatives *isonitroso*-compounds, it would have been far better had Victor Meyer chosen the appropriate and expressive name of *hydroximido*-compounds, and the terminal *hydroximide* instead of the inexpressive although shorter *oxim*.

Dr. Divers, however, I think makes a somewhat similar mistake. Nitrous acid, and not its anhydride, must be the active agent, and therefore we may write his equation in the following manner, without affecting the formula which he deduces:

$$\begin{matrix}HO.NO\\HO.NO\end{matrix} + \begin{matrix}CH_2\\CH_2.OH\end{matrix} = \begin{matrix}HO.N{:}CH\\HO.N{:}C.OH\end{matrix} + OH_2$$

$$\begin{matrix}HO.N{:}CH\\HO.N{:}C.OH\end{matrix} = OH_2 + O\begin{matrix}.N{:}CH\\.N{:}C.OH\end{matrix}$$

Here it is assumed that the CH_2-group exchanges 2H for N.OH, a reaction which, so far as I am aware, is as entirely without precedent as that involving the exchange of H in CH_3 or CH_2 for NO under the influence of nitrous acid; the conversion of nitromethane into "methylnitrolic acid" might indeed be cited, but can scarcely be regarded as a parallel case.

Whatever may be the force of this objection, I am led to propound a different formula on what I consider to be far higher grounds, viz., from a consideration of what is probably the nature of the reaction between alcohol, nitric acid and mercury.

In the first place, it is not probable that the fulminate is the immediate product of the action of nitrous acid, however produced, upon alcohol. It is well known that when treated with dilute nitric acid, alcohol undergoes *hydroxylation*, being finally converted into "orthoxalic acid," $C(OH)_3.C(OH)_3$, and Dr. Debus's classical research leaves little doubt that one by one the hydrogen-atoms are displaced by hydroxyl; in this way, the alcohol is converted first into "ethaldehydrol" (comp. *Miller's Chemistry*, vol. iii, 5th ed., pp. 504, 715), and then probably into "hydroxyethaldehydrol":—

$CH_3.CH_2(OH)$	$CH_3.CH(OH)_2$	$CH_2(OH).CH(OH)_2$
Ethyl alcohol.	Ethaldehydrol.	Hydroxyethaldehydrol.

This last-mentioned compound I am inclined to regard as the primary source of the fulminate, *which is formed from it by the simultaneous—or it may be consecutive—action of nitrous acid and hydroxylamine:*

$$\begin{matrix}HO.NO\\HO.NH_2\end{matrix} + \begin{matrix}H_2C.OH\\HC(OH)_2\end{matrix} = \begin{matrix}HO.N.C.OH\\HC(N.OH)\end{matrix} + 2OH_2.$$

Hydroxyethaldehydrol.

$$\begin{matrix}HO.N.C.OH\\HC(N.OH)\end{matrix} = \begin{matrix}ON.C.OH\\\diagdown C(N.OH)\end{matrix} + OH_2.$$

Fulminic acid.*

* This formula is obviously not the only one which could be deduced, assuming the fulminate to be formed in the manner suggested.

That hydroxylamine may be formed by reduction of nitric or nitrous acid by ethaldehydrol, or more highly hydroxylised derivatives of alcohol, is in the highest degree probable, especially after Dr. Divers' recent communication on the production of hydroxylamine in the dissolution of metals by nitric acid.

The formula which I now propose differs but slightly from that previously brought forward, but it is a far better expression of our knowledge of the fulminates. The representation of the carbon-atoms as exercising "triad" instead of "diad"* functions certainly removes an obvious objection to my earlier formula.

Steiner's formula is inadmissible, both because, as Dr. Divers also remarks, it is a symmetrical expression, and because it is improbable that a *hydroximide* would furnish *nitro*trichloromethane; this, however, it is proposed to test experimentally, and I shall also endeavour to prepare fulminates by operating in accordance with the hypothesis here put forward.

In the following paper "On Liebig's Production of Fulminating Silver without the Use of Nitric Acid," which has been received since this note was written, Dr. Divers and Mr. Kawakita show that even nascent nitrous acid, alcohol and a silver salt do not yield fulminate, and that nothing but an energetic oxidation of the alcohol by a mixture of nitric acid and either mercury or silver nitrate seems to be effective. This is entirely in accordance with the view which I here put forward.

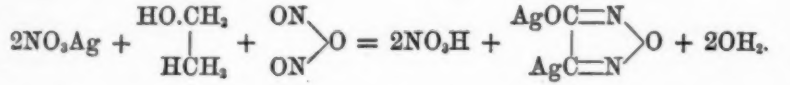
V.—*On Liebig's Production of Fulminating Silver without the Use of Nitric Acid.*

By Edward Divers, M.D., and Michitada Kawakita, M.E.

According to Liebig (*Ann. Pharm.*, **5**, 287; *Gmelin's Handbook*, Organic Chemistry, English edition, **3**), fulminating silver separates in large needles, and without ebullition of the liquid, when nitrous acid is passed into an alcoholic solution of silver nitrate. This reaction so greatly simplifies the problem as to what is the essential part of the complex changes occurring when hot alcohol and a nitrous-nitric acid solution of silver are mixed, in the formation of

* These expressions have reference to the definition of valency which, following Lossen, I prefer, viz., that a radicle is monad, diad, triad (univalent, bivalent, trivalent), according as it is in direct association with either one, or two, or three radicles, &c.

silver fulminate, that it has been repeatedly adduced for this purpose. Divers himself, in our recent communication to the Society on the fulminates, felt called upon to show that his view of their constitution was in accordance with that reaction, and indeed found it well fitted for the purpose, thus:—



But such a reaction presents the first example of the displacement by isonitrosyl (—NO—) of the hydrogen of the group $—CH_3$, this having hitherto been effected only in the group $=CH_2$; and, as another peculiarity, presents an example of the formation of an isonitrosyl-compound by the action of nitrous anhydride in a neutral solution, instead of in a solution of nitrite at first alkaline and then made acid. There is thus, but for Liebig's statement, an improbability of its really happening, and it is therefore not so surprising as it might have been that, having tried the experiment, we have failed to verify Liebig's statement.

Silver nitrate being only sparingly soluble in alcohol, we used saturated solutions of it in alcohol of 0·83 sp. gr., with a little solid nitrate at the bottom of the vessel. We passed nitrogen trioxide for long and for short intervals into the solution. The gas was fully absorbed, the liquid became warm, the small excess of silver nitrate dissolved, and much nitrous ether evaporated. No effervescence occurred, and gradually, the volume of the solution sensibly diminishing, needle-shaped crystals were deposited on the bottom and sides of the flask during the passage of the gas. But these crystals were only silver nitrate mixed with a very small quantity of some organic silver salt, not fulminate, which we have not succeeded in identifying yet. We conclude, therefore, that the behaviour of alcohol towards nitrogen trioxide is in no way altered by the presence of silver nitrate, and that we must look rather to the nitric acid or silver nitrate present in the ordinary mixture used for the preparation of the fulminate, as the source of the isonitrosyl radical.

It was difficult for us to come to believe Liebig wrong, even though our own results seemed to us more likely than his, and others will perhaps test the matter before accepting our statement. In the meantime we may be allowed to remind chemists that when Liebig did his celebrated work on the fulminates the analysis of these bodies was a matter of serious difficulty, and that he consequently never even made a satisfactory analysis of mercury fulminate, getting for the mercury only the widely-wrong number 56·9 per cent. instead of 70·4; while the substance, which under two forms he described as copper

fulminate, is stated by Pagenstecher (*Gmelin's Handbook*) to contain but very little copper, and not to be the fulminate. Then, concerning the production of silver fulminate by nitrous acid, nothing more than we have given is stated in *Gmelin*, and this comes in the section headed "Formation," no word of the method being found under the heading "Preparation."* It may therefore be assumed with probability that crystals of silver nitrate, such as we got in the ordinary course of the experiment, were taken by him for the fulminate without further examination.

We have prepared silver fulminate by the ordinary method of adding to alcohol a nitric acid solution of silver still charged with the nitrous acid arising from the dissolution of the metal; and then, again, by adding an exactly equivalent solution made with silver nitrate and nitric acid, but without any nitrous acid. Both operations were highly successful, and as a matter of fact, whatever may have been the cause, the one without the nitrous acid gave a decidedly better yield than the one with it. In his directions for preparing mercury fulminate, Liebig recommends the dissolution of the mercury to be performed in a capacious flask, and the mixture afterwards with the alcohol to be poured back into this flask, in order to absorb the nitrous gas it contains. Whether his directions were dictated merely by his belief that nitrous acid played an essential part, or by his actual experience as to the yield of mercury fulminate obtained, cannot now be told. But if we assume that he had such a belief, it is not difficult to suppose that having concluded, as we ourselves did at first, that crystals of silver nitrate, unexpectedly appearing as they did, were the fulminate, he did not further examine them.

We have made some experiments with silver nitrite. In these we at first avoided the addition of silver nitrate or of nitric acid, but as we then got only negative results, and the use of these is much more convincing as to the correctness of what we have found, we need not detail that part of our work. A mixture of silver nitrate and silver nitrite was added to alcohol, and nitric acid, sp. gr. 1·35, then dropped in with shaking. The silver nitrite, which is nearly insoluble, promptly dissolved in the alcohol in proportion as the acid was added, and without any effervescence. A strong odour of ethyl nitrite was given off, but no fulminate was obtained, although here we did expect success; and it would seem from this that even nascent nitrous acid, alcohol, and a silver salt do not yield fulminate. Nothing but an energetic oxidation of the alcohol by a mixture of nitric acid and either mercury or silver nitrate seems to be effective.

* Here in Japan we cannot consult Liebig's own account.

Attempts to form Fulminating Copper.

From the similarity of copper to mercury and silver in its relations towards nitric acid, recently discussed by Divers in his paper on "Hydroxylamine" in this Journal, we have been induced to make several trials to prepare copper fulminate from alcohol, and either copper nitrate and nitrogen trioxide; or copper nitrate and nitric acid; or copper nitrate, nitric acid, and nitrous acid—all with entire absence of success.

The active catalytic oxidising power of cupric salts, which affects the action of nitric acid upon copper (Acworth and Armstrong), and so readily causes the destruction of hydroxylamine (or isonitrosyl hydride), is sufficient to explain the failure. In proof of its being exerted in this case, we can state that when nitrogen trioxide is passed for some time into an alcoholic solution of copper nitrate, an abundant precipitation of copper *œxalate* is produced without any evident activity of the nitrous anhydride, which all along becomes quietly absorbed by the alcohol.

VI.—*The Illuminating Power of Ethylene when Burnt with Non-luminous Combustible Gases.*

By Percy F. Frankland, Ph.D., B.Sc., Assoc. R.S.M., Demonstrator of Practical Chemistry in the Normal School of Science and Royal School of Mines, South Kensington.

In the year 1878 Frankland and Thorne (*Chem. Soc. J.*, **33**, 89) published the results of their investigation "On the Luminosity of Benzol when Burnt with Non-luminous Combustible Gases." Their results constitute the first and only accurate contribution to our knowledge of the influence which the non-luminous constituents of coal-gas exert upon its illuminating power. Although this subject is of such obvious importance in connection with the theory of artificial lighting, nothing further has, to my knowledge, been attempted in the same direction.

The luminiferous hydrocarbon selected for investigation, in the present research, was ethylene, which, owing to its gaseous state,

admitted of being more exhaustively experimented on than the liquid benzene. Moreover since the illuminating power of coal- and cannel-gas is chiefly due to ethylene and its analogues, the results obtained with this gas are of greater practical interest than those with the vapour of benzene, which exists in only very small quantity in coal-, and in still smaller quantity in cannel-gas. And again, whereas the illuminating power of pure olefiant gas can be directly determined, all attempts to do this in the case of benzene proved abortive.

Great care was taken to obtain all the gases employed in the purest state practicable. The methods adopted for their preparation were the following:—

Preparation of Ethylene.—A mixture of 25 parts by weight of rectified methylated spirit and 150 parts of strong sulphuric acid was heated in a flask. By covering the bottom of the flask with sand, all inconvenient frothing was prevented, and by adding, through a stoppered funnel, a further quantity of the above mixture, to which an equal volume of methylated spirit had been added, a rapid and continuous current of ethylene could be maintained for many hours. The gas so produced was first passed through a Woulff's bottle containing strong sulphuric acid to arrest any vapour of alcohol or ether; it was then passed in succession up two eprouvettes charged with dry slaked lime to absorb carbonic and sulphurous anhydrides, then through two bottles containing a strong solution of caustic soda, and finally through another bottle filled with pumice soaked in oil of vitriol. The gas so purified was then collected in a holder filled with water, recently boiled to prevent admixture with dissolved air. The gas so collected was found, on analysis, to be almost pure ethylene:—

CO_2	0·05
O	0·94
C_2H_4	97·52
N	1·49
	100·00

Preparation of Hydrogen.—The hydrogen used was obtained by the action of dilute sulphuric acid on zinc, the gas being passed through a strong solution of caustic soda, and collected in a gas-holder as above.

Preparation of Carbonic Oxide.—This gas was obtained in a state of purity by heating together powdered potassic ferrocyanide and concentrated sulphuric acid, passing the gas through a solution of caustic soda and a lime-scrubber, as in the preparation of ethylene.

Preparation of Marsh-gas.—The ordinary method of preparing

marsh-gas, by the distillation of sodic acetate with soda-lime, yields, except on rare occasions, a very impure product. The crude gas I found on one occasion to contain about 6 per cent. of constituents which could be absorbed by fuming sulphuric acid. After purifying the crude gas by passing a slow stream of it through bromine, then through a saturated solution of caustic soda, and finally through a lime-tower, I obtained an almost non-luminous gas, which, on one occasion, was nearly pure marsh-gas, but on another occasion was mixed with a considerable proportion of hydrogen. The following analyses show the constitution of the purified gas obtained on two different occasions:—

CO_2	0·00	0·26
O	0·30	0·48
C_nH_{2n}, &c	—	0·24
H	3·79	13·75
CH_4	91·82	82·83
N	4·09	2·44
	100·00	100·00

The determinations of illuminating power recorded in this paper were in all cases made with pure marsh-gas prepared by decomposing zinc-methyl with water. As this is the first time that, to my knowledge, marsh-gas has been prepared in large quantities by this method, a fuller description of the apparatus employed for the purpose may be of some interest.

The zinc-methyl was prepared by heating to a temperature of 100—120° C., by means of an oil-bath, a mixture of 9 ounces of methylic iodide and 6 ounces of dry ether with an excess of granulated zinc in a digester of wrought copper (Frankland, *Phil. Trans.*, 1859, vol. **149**; *Proc. Roy. Soc.*, **9**, 678). The digestion was carried on at this temperature for about 24 hours. In this operation great care has to be taken that all the ingredients employed are perfectly dry, the presence of a little moisture in the digester causing the internal pressure to rise to such an extent that the leaden washer by which the digester is sealed may give way. This on one occasion actually took place: a piece of the washer was projected with great violence, breaking a window some distance off; a large volume of zinc-methyl was discharged into the room, and immediately burst into flame, whilst the force of this sudden escape threw the oil-bath and digester to the ground. I, although reading the temperature of the bath at the time, escaped without any injury whatever.

After the digester was cool, the screws at the top were eased, and the gas within allowed to blow off before actually removing the cap.

After removing the cover, the digester was closed with a cork fitted with a thermometer and wide delivery-tube, and then heated in an oil-bath. The delivery-tube, which was about 4 feet in length, passed at its lower extremity through the cork of a receiver immersed in ice, and half filled with well-dried sand. The distillation was carried on as long as any volatile matter came off from the digester, the distillate consisting of zinc-methyl and ether becoming absorbed by the sand in the receiver.

The mouth of the receiver was then fitted with a cork bearing a dropping-funnel and wide delivery-tube. By means of the dropping-funnel water was added to the contents of the receiver, each drop of water occasioning a violent effervescence due to abundant evolution of marsh-gas. The marsh-gas was carried off by the delivery-tube, and passed first through a Woulff's bottle containing a saturated solution of caustic soda in methylated spirit, to absorb the vapour of any methylic iodide that had escaped decomposition in the digester, then through two Woulff's bottles filled with pumice soaked in oil of vitriol to absorb the ether-vapour, after which it was collected in a gas-holder filled with recently boiled water. The marsh-gas so collected was always found to contain a trace of the vapour of methylic iodide, which had escaped absorption owing to the violence with which the gas is disengaged in the action of water upon zinc-methyl. In order to remove this trace of methylic iodide, which might have exerted an important influence upon the illuminating power of the marsh-gas, a slow current of the gas was made to pass from the gas-holder through a Woulff's bottle containing alcoholic soda, through another filled with pumice saturated with oil of vitriol, and then through a series of about 15 bulbs containing antimony pentachloride, and finally through another Woulff's bottle containing caustic soda before being collected in a gas-holder. The gas so obtained was found to be absolutely pure marsh-gas mixed with a very small proportion of oxygen and nitrogen; on analysis it gave results leading to the following percentage composition:—

CH_4	95·99
O	1·51
N	2·50
	100·00

Determination of Illuminating Power.—The illuminating power of the gases was determined by means of Evans' photometer, the gas being burnt from a Sugg's argand, known as the "Referee's Burner," with the chimney prescribed by the Board of Trade for the testing of 16-candle gas. In obtaining the lower illuminating values, a single

standard candle was employed, whilst in the case of the higher values two standard candles were necessary.

A sample of the gas was always taken at the time, and subsequently submitted to analysis.

In all cases a current of the gas under examination was passed through the meter, and no photometric observations recorded until the luminosity of the flame was constant or nearly so. The values adopted are in all cases the mean of at least ten observations, and corrected to 5 cubic feet of gas and 120 grains of spermaceti consumed per hour.

Illuminating Power of Ethylene.—On taking the mean of the four determinations recorded below, I found 68·5 candles to be the illuminating power of pure ethylene when consumed at the rate of 5 cubic feet per hour:—

Experiment.	Candles observed.	Rate.		Candle-power, corrected to 5 cubic feet of gas and 120 grains of spermaceti per hour.
		Gas in cubic feet per hour.	Candles in grains per hour.	
I.	27·00	1·96	117	67·2
II.	36·96	2·22	102	70·7
III.	34·28	2·44	117	68·5
IV.	34·40	2·22	105	67·7
				4) 274·1
			Mean	= 68·5

The luminosity of ethylene being thus fixed, the diminution of its illuminating power by the admixture of increasing proportions of hydrogen, carbonic oxide, and marsh-gas respectively, was then determined.

The illuminating power of these mixtures is recorded graphically in the accompanying diagram, in which the ordinates represent the percentages of ethylene, and the abscissæ the luminosity in standard candles. By joining in the diagram the points which were found by experiment, a broken line, shown in black, is obtained in the case of each gas, whilst in each instance a line, distinguished by dashes or crosses, has been drawn, showing the probable course of the curve, thus:

Hydrogen ..... — — — — — —
Carbonic oxide .... | | | | | |
Marsh-gas ..... × × × × × ×

From these curves those marked with dots between the dashes or crosses, *e.g.*, — . — . —, are calculated to indicate the illuminating power of the mixture when 5 cubic feet of ethylene per hour are burnt irrespectively of the proportion of the diluent. These dotted curves are of perhaps more interest than the others, inasmuch as they show how the *intrinsic illuminating power* of the ethylene is affected by the nature and proportion of the diluent.

Illuminating Power of Ethylene when mixed with Hydrogen.—The luminosity of mixtures of ethylene and hydrogen shows an almost uniform diminution from 68·5 candles, when the gas consists wholly of ethylene, to zero, when the mixture is composed of 10 parts of ethylene and 90 parts of hydrogen. Thus the following experimental results were obtained:—

Percentage.		Candles observed.	Rate.		Candle-power, corrected to 5 cubic feet of gas and 120 grains of spermaceti per hour.
C_2H_4.	H.		Gas in cubic feet per hour.	Candles in grains per hour.	
77·55	22·45	28·04	2·50	116·8	54·58
68·39	31·61	27·86	2·65	112·5	49·37
53·58	46·42	25·00	3·56	133·8	39·21
35·47	64·53	32·76	5·38	121·6	30·85
26·08	73·92	29·00	5·82	110·0	22·84
13·37	86·63	13·96	10·00	115·7	6·73

On referring to the curve for hydrogen in the diagram, it will be seen that although the experimental line falls away towards the left, the curve, calculated for a uniform consumption of 5 cubic feet of ethylene per hour, actually passes somewhat to the right in the first instance, the intrinsic luminosity of the ethylene experiencing no diminution until after the proportion of hydrogen has risen to about 70 per cent., after which it rapidly falls to zero when the hydrogen reaches 90 per cent. of the mixture. The rapid diminution in the *intrinsic* luminosity of the ethylene thus takes place at a point at which the mixture is, as regards the proportion of carbon to hydrogen, equivalent to CH_4 or marsh-gas.

It was first pointed out by Dittmar (*Chem. News*, **34**, 145) that a mixture of ethylene and hydrogen containing only 10 per cent. of the former, possesses practically no illuminating power; but Dittmar also states that a mixture of the same gases, containing 25 per cent. of ethylene, has about the same luminosity as marsh-gas; now this is the case only when the gas is burnt from a fishtail burner, for with

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an argand burner it can be made to yield a light of about 20 candles, as indicated in the diagram.

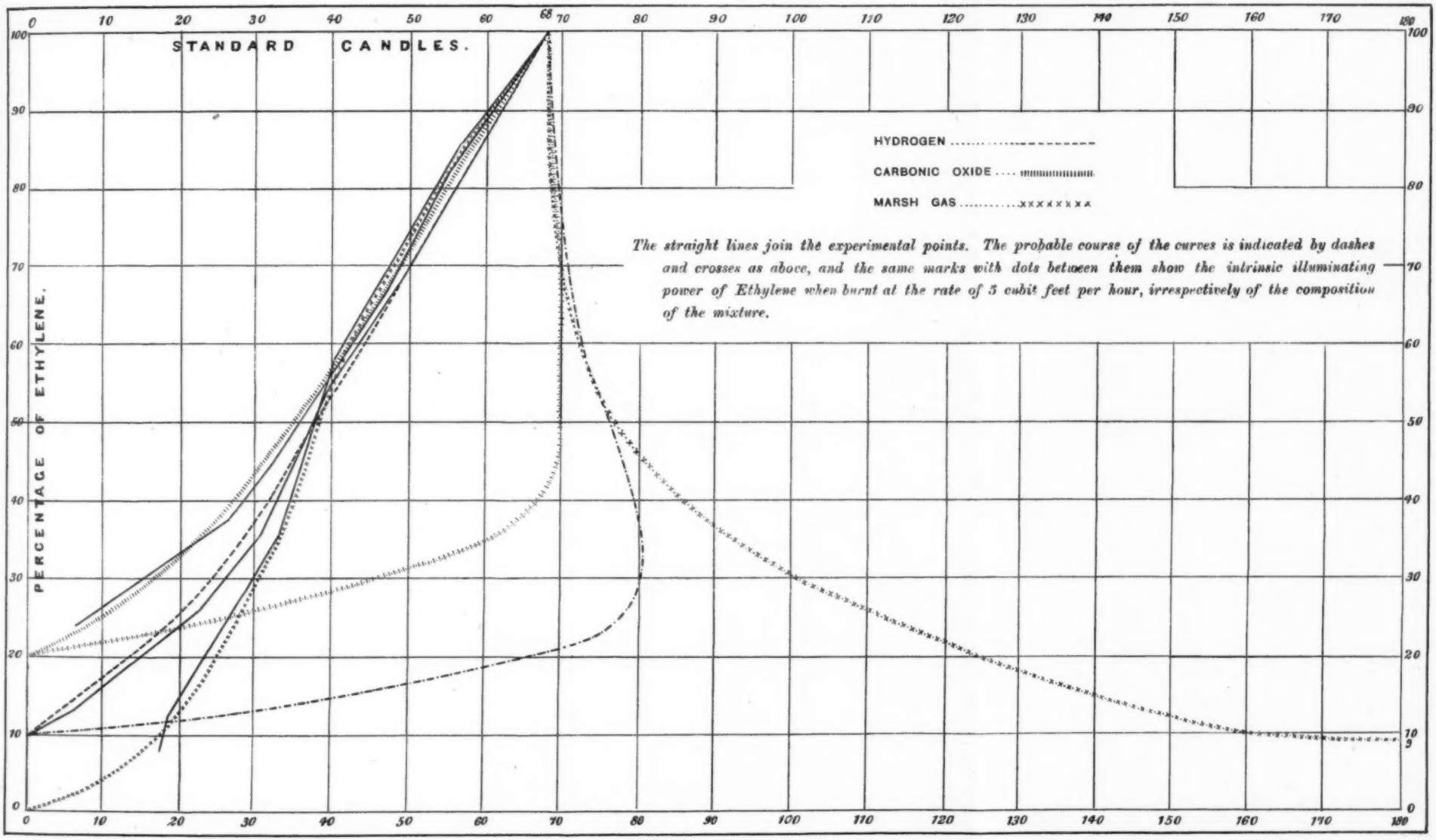
The results obtained with ethylene and hydrogen, on being compared with those of Frankland and Thorne, with benzolised hydrogen, show that the illuminating power of a mixture of benzene and hydrogen is considerably greater than that of a mixture of ethylene and hydrogen containing the same proportion of carbon-vapour. Thus, 1 per cent. of benzene, C_6H_6, is equivalent to 3 per cent. of ethylene, C_2H_4. Now, Frankland and Thorne found that a mixture of benzene and hydrogen, containing 7·6 per cent. of benzene, equivalent to 22·8 per cent. of ethylene, gave the light of 26·41 candles when 5 cubic feet of the mixture were consumed per hour, whilst the illuminating power of a mixture of 22·8 per cent. of ethylene and 77·2 per cent. of hydrogen would, as seen from the diagram, be only about 17 candles. The results are, however, not strictly comparable, as Frankland and Thorne employed a fishtail burner in their experiments; had the same burner been used in both cases, the difference in illuminating power would doubtless have been even still more striking.

Illuminating Power of Ethylene when mixed with Carbonic Oxide.—The following experimental results were obtained with mixtures composed of varying proportions of ethylene and carbonic oxide:—

Percentage.		Candles observed.	Rate.		Candle-power, corrected to 5 cubic feet of gas and 120 grains of spermaceti.
Ethylene.	Carbonic oxide.		Gas in cubic feet per hour.	Candles in grains per hour.	
81·65	18·35	29·40	2·54	114·50	55·27
67·75	32·25	29·00	2·92	115·50	47·73
46·30	53·70	31·98	4·18	103·75	33·09
37·94	62·06	30·16	5·15	108·75	26·52
28·73	71·27	15·76	5·45	111·00	13·36
23·89	76·11	7·16	5·33	117·25	6·56

Thus, in every case the illuminating power of mixtures of ethylene and carbonic oxide was found to be less than that of corresponding mixtures of ethylene and hydrogen, the inferior luminosity of the mixtures containing carbonic oxide becoming more marked as the proportion of ethylene diminishes. In consequence of this, the curve representing the intrinsic illuminating power of ethylene with carbonic oxide (marked thus | . | . | in the diagram) lies wholly to the left of the corresponding curve for hydrogen. This curve shows

ILLUMINATING POWER OF ETHYLENE WHEN MIXED WITH COMBUSTIBLE DILUENTS.


STANDARD CANDLES.
PERCENTAGE OF ETHYLENE.
HYDROGEN
CARBONIC OXIDE
MARSH GAS
The straight lines join the experimental points. The probable course of the curves is indicated by dashes and crosses as above, and the same marks with dots between them show the intrinsic illuminating power of Ethylene when burnt at the rate of 5 cubic feet per hour, irrespectively of the composition of the mixture.

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that the intrinsic luminosity of the ethylene suffers no very marked diminution until a proportion of about 60 per cent. of carbonic oxide is reached. After this the illuminating power rapidly sinks until a proportion of 80 per cent. of carbonic oxide is attained, when the mixture practically ceases to be luminous at all.

Illuminating Power of Ethylene when mixed with Marsh-gas.—The following experimental results were obtained with mixtures composed of varying proportions of ethylene and marsh-gas:—

Percentage Composition.		Candles observed.	Rate.		Candle-power, corrected to 5 cubic feet of gas and 120 grains of spermaceti.
C_2H_4.	CH_4.		Gas in cubic feet per hour.	Candles in grains per hour.	
85·67	14·33	24·82	2·14	120·0	57·91
69·09	30·91	24·20	2·27	108·0	47·88
57·74	42·26	21·50	2·46	111·0	40·42
35·90	64·10	20·60	2·59	100·0	33·17
13·00	87·00	13·72	3·33	112·8	19·35
7·87	92·13	14·26	3·45	102·0	17·59

From these figures, and the curve in the diagram constructed therefrom, it will be seen that those mixtures which are rich in ethylene have about the same luminosity as corresponding mixtures of ethylene with hydrogen and carbon oxide respectively, whilst the illuminating power of mixtures richer in marsh-gas greatly exceeds that of corresponding mixtures containing hydrogen or carbonic oxide. The marsh-gas curve, in fact, which starts at about the same angle as the curves for hydrogen and carbonic oxide, gradually approaches the perpendicular as the proportion of marsh-gas increases.

The diagram also shows that the intrinsic luminosity of the ethylene, as calculated for a uniform consumption of 5 cubic feet of ethylene per hour, continually increases, and that very rapidly, for mixtures containing upwards of 50 per cent. of marsh-gas. Thus the ethylene in a mixture containing 92 per cent. of marsh-gas gives a light of 175 candles, calculated for 5 cubic feet of ethylene consumed per hour.

That an increase in the intrinsic luminosity of ethylene takes place when the latter is burnt with a large proportion of suitable diluents is seen from the illuminating power of coal-gas. Thus, an analysis I have recently made of the London gas shows it to contain 4·51 per cent. of illuminating hydrocarbons, which from their carbon-density, 2·87, are equivalent to 6·46 per cent. of ethylene; now the London gas has an illuminating power of 16 candles when 5 cubic feet of gas

per hour are burnt from the same burner as that used in these experiments, so that the intrinsic luminosity of the ethylene in this gas, calculated for 5 cubic feet of ethylene consumed per hour, is 247 candles. The higher intrinsic value obtained for the condensable hydrocarbons in coal-gas is due to the latter being partially composed of benzene and other hydrocarbons of greater density than ethylene, and possessing a higher illuminating power than their equivalent of ethylene. Indeed, it is only by recognising the greater value of marsh-gas as a diluent that the illuminating power of coal-gas can be satisfactorily accounted for. From analyses which I have recently made of a number of different coal- and cannel-gases, I find that the quantity of benzene present in ordinary gas must be very small indeed, as the carbon-density of the condensable hydrocarbons is almost invariably less than 3; to what source then can the 16-candle light of a gas such as that supplied to London, which contains the equivalent of 6·46 per cent. of ethylene, be referred? If this proportion of ethylene be mixed with hydrogen, it is almost non-luminous, whilst if mixed with equal volumes of hydrogen and marsh-gas, as in coal-gas it practically is, it will, according to the diagram, give a light of about 7 candles, thus leaving only 9 candles more to be accounted for by the presence of the hydrocarbons of greater density than ethylene.

Frankland and Thorne also found that the intrinsic luminosity of the vapour of benzene was very much greater when burnt with marsh-gas, than when mixed with the same proportion of either hydrogen or carbonic oxide.

That mixtures of ethylene and marsh-gas possess a greater illuminating power than corresponding mixtures of ethylene and hydrogen, and these again a higher luminosity than similar mixtures of ethylene and carbonic oxide, receives perhaps a partial explanation in the greater absolute thermal effect of marsh-gas than that of hydrogen, and of hydrogen than of carbonic oxide. Thus according to Favre and Silbermann, the combustion of—

1 mol. (= 2 grams) of	hydrogen	yields 68,924	heat-units.
„	carbonic oxide	„ 67,284	„
„	marsh-gas	„ 209,008	„

The actual pyrometric effects of these gases when burnt in air have never been determined, and their calculation is attended with much uncertainty, owing to our ignorance of the specific heat of gases at high temperatures. According to Bunsen (*Pogg. Ann.*, 1867), however, the temperature obtained in the case of carbonic oxide lies between 1909° and 2084°, whilst in the case of hydrogen it is stated to be 2024°. Berthelot (*Ann. Chim. Phys.* [5], **12**, 309), on

the other hand, gives the temperature for carbonic oxide as lying between 2200° and 1750°, and that for hydrogen between 2100° and 1700° If these calculated temperatures really approximate to those actually obtained in combustion, the relative illuminating power of the mixtures in question is evidently not wholly dependent upon the temperature of the flame.

It is also most probable that at the high temperature of the flame obtained with the argand burner, the marsh-gas may possess a very appreciable illuminating power of its own. Indeed it has been shown (Frankland, *Journ. of Gas Lighting*, 1867) that marsh-gas burns with a flame of considerable luminosity when heated to about 300° along with the air necessary for its combustion. I find, moreover, that marsh-gas prepared from sodic acetate and purified by bromine, as described, possesses a very decided illuminating power of its own, amounting to several candles, when burnt from a Referee's burner, whilst from a fish-tail burner it emits but a very feeble light. I conclude from this that the increase in illuminating power, which is observed when coal-gas is burnt from a Referee's burner, is partly due to the light thereby obtained from the marsh-gas, which with a fish-tail burner produces practically no luminous effect.

The results I have obtained may be thus briefly summarised :—

(1.) That pure ethylene, when burnt at the rate of 5 cubic feet per hour from a Referee's argand burner, emits a light of 68·5 standard candles.

(2.) That the illuminating power of equal volumes of mixtures of ethylene with either hydrogen, carbonic oxide, or marsh-gas is less than that of pure ethylene.

(3.) That when the proportion of ethylene in such mixtures is above 60 per cent., the illuminating power of the mixture is but slightly affected by the nature of the dilutent. When, on the other hand, the proportion of ethylene in such mixtures is low, the illuminating power of the mixture is considerably the highest when marsh-gas is the diluent, and the lowest when the ethylene is mixed with carbonic oxide.

(4.) That if 5 cubic feet of ethylene be uniformly consumed irrespectively of the composition of the mixture, the calculated illuminating power is in every case equal to or actually greater than that of pure ethylene until a certain degree of dilution is attained. This intrinsic luminosity of ethylene remains almost constant when the latter is diluted with carbonic oxide, until the ethylene forms only 40 per

cent. of the mixture, after which it rapidly diminishes to zero, when the ethylene forms only 20 per cent. of the mixture. When the ethylene is diluted with hydrogen, its intrinsic luminosity rises to 81 candles when the ethylene constitutes 30 per cent. of the mixture, after which it rapidly falls to zero when the ethylene amounts to only 10 per cent. In the case of mixtures of ethylene and marsh-gas, the intrinsic luminosity of the former is augmented with increasing rapidity as the proportion of marsh-gas rises, the intrinsic luminosity of ethylene, in a mixture containing 10 per cent. of the latter, being between 170 and 180 candles.

I hope very shortly to be able to communicate the results of my experiments on the illuminating power of hydrocarbons when burnt with incombustible diluents.

VII.—*Researches on the Gums of the Arabin Group.* Part I. *Arabic Acid; its Composition and the Products of its Decomposition.*

By C. O'Sullivan.

The chief constituent of gum arabic, arabic acid, has been the subject of many investigations. In *Gmelin* (**4**, 1, 639; English edition, **15**, 194) there are references to nineteen investigators, and several additions could be made. Of all these, the works of Neubauer (*J. pr. Chem.*, **62**, 193; **71**, 255) and Mulder (*Bull. de N.*, 1838, 167) seem to be the most important. Without going into detailed criticisms of the individual works, the chief outcome of all is, that arabic acid is a $C_{12}H_{22}O_{11}$ body; but, in the face of Mulder's numbers and of Neubauer's analyses of the potassium, barium, and calcium salts, it is difficult to understand how this formula has retained its place in the literature. One analysis of the lime salt by Neubauer leads, according to himself, to the formula $C_{72}H_{120}O_{60}CaO$, and another to $C_{24}H_{40}O_{20}CaO$; one of these, if not both, was alkaline, and it is easily seen that neither can be looked upon as a pure body; in fact, no attempt appears to have been made to make them such. The mean of Neubauer's analyses of the free acid leads to $C_{12}H_{22}O_{11}$, yet he takes $nC_6H_{10}O_5$ as its composition in the salts. Berthollet, Saussure, Guerin-Varry, and Mulder give numbers which, although they differ considerably amongst themselves, make a close approximation to those required by $nC_6H_{10}O_5$. More recently Scheibler (*Ber.*, **6**, 620) gives analyses of a gum acid prepared from beet, which, he says, is identical with arabic acid. The mean of his numbers leads to the formula $C_{12}H_{22}O_{11}$, but he himself is evidently not satisfied with the results. Finding the literature so unsatisfactory, and wishing to learn something definite of the body, I decided to make a fresh examination of it. This examination is still incomplete; nevertheless, the results so far obtained are of sufficient interest to admit of being recorded.

Gum arabic, ordinary Levantine gum, is stated to be a salt of arabic acid with potassium, magnesium, and calcium. The sample of this body that first came to my hands contained 13·8 per cent. water and 3·0 per cent. ash, consisting of potassic, magnesic, and calcic carbonates. In separating the arabic acid, I have not deviated materially from the method employed by Neubauer. The gum is dissolved in as little water as possible, and any insoluble matter allowed to settle. The clear liquid is then decanted off, twice or thrice as much hydrochloric acid as is sufficient to convert the bases into chlorides is added, and arabic acid then precipitated out of the solution by an

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excess of alcohol. The curdy precipitate is well washed with spirit, and then pressed as free from it as possible. It is dissolved in boiling water, the solution left to cool, and alcohol is gradually added, with continual stirring, care being taken to avoid adding too much at once. In this way the liquid becomes quite milky without the formation of a precipitate, but the addition of a few drops of hydrochloric acid immediately "breaks" the milk, producing a curdy precipitate, which, by care in the addition of the acid, can be thrown out in successive fractions. I divided the quantity with which I worked into four parts, which I shall call precipitates 1, 2, 3, and 4, according to the order in which they were obtained. I did this in order to determine if it were possible to break up the material into two or more different bodies. Each precipitate was several times dissolved and reprecipitated, and was then dehydrated with absolute alcohol, pressed, and dried over sulphuric acid. The bodies thus obtained are white, friable, soluble in water, and free from ash; their solutions are acid. My first object was to determine whether the four portions were identical. I found them to be lævorotatory, and, in solutions containing 5 to 6 grams of dry substance in 100 c.c., the optical activity was—

1st precipitate,	$[\alpha]_j =$	$-26{\cdot}3°$
2nd „	$[\alpha]_j =$	$-25{\cdot}7$
3rd „	$[\alpha]_j =$	$-26{\cdot}7$
4th „	$[\alpha]_j =$	$-27{\cdot}0$

A portion of each was dissolved in water, and exactly neutralised with baryta-water. To the clear concentrated solution of barium salt alcohol was added as long as a precipitate formed. This curdy precipitate was washed with alcohol, treated with absolute alcohol, pressed, and dried over sulphuric acid. Dried *in vacuo* and afterwards in a current of dry air at 100°, the barium salt from the

1st precipitate was found to contain				5·96	per cent.	BaO.
2nd	„	„	„	6·00	„	„
3rd	„	„	„	6·07	„	„
4th	„	„	„	5·90	„	„

These results, coupled with the optical activity determinations, show clearly that, in this case at least, we have to deal with a homogeneous body.

According to Scheibler, the products of the action of sulphuric acid on arabic acid are a crystallisable sugar, a non-crystallisable one, and an acid of which the barium salt is insoluble in alcohol. He does not describe the barium salt more particularly. Kiliani (*Ber.*, **15**, 33) confirms Scheibler's statement. Now, it seemed to me possible

that a careful examination of this acid and of the other products of the action of sulphuric acid on arabic acid would throw some light on the nature and composition of arabic acid itself. If, I reasoned, arabic acid is as large a molecule as the small proportion of barium oxide it is capable of neutralising indicates it to be, it is possible that, under the influence of sulphuric acid, it will behave somewhat after the manner in which I have shown starch to behave (*Chem. Soc. J.*, 1876 [ii], 125). It will possibly yield acids of gradually diminishing molecular weight, and a sugar or sugars. From this idea to the test was no great distance.

500 grams of arabic acid ($[\alpha]_j = -27°$) free from ash, were dissolved to 1500 c.c. solution, and 40 grams of sulphuric acid in 150 c.c. water added. This mixture was boiled three hours, cooled, and exactly neutralised with a hot solution of baric hydrate. The barium sulphate was filtered out, the bright filtrate evaporated to 1000 c.c. or thereabouts, and alcohol, sp. gr. 0·83, added as long as a precipitate formed. This precipitate was waxy, like dextrin, and was easily separated from the supernatant liquid. It was repeatedly dissolved in water and reprecipitated with alcohol to free it from sugar, and lastly treated with absolute alcohol, and dried over sulphuric acid. Thus dried, it is a white friable body. After remaining in a vacuum over sulphuric acid for some time, it soon became constant in weight when submitted at 100° to a current of dry air. The dry substance yielded 14·57 per cent. BaO. This, in itself, was sufficient to show that the arabic acid molecule had been broken down; a further examination was necessary to determine whether this product was homogeneous. A known weight of it was dissolved in the least possible quantity of water, and sufficient sulphuric acid added to precipitate two-thirds of the barium. The barium sulphate was filtered out, and the filtrate concentrated, in small portions, to a syrup. Sufficient alcohol was added to this to produce a moderate syrupy precipitate, which was allowed to subside: we shall call it, precipitate *a*. The alcoholic supernatant liquid was decanted off, and a quantity of clear hot baryta-water, sufficient to neutralise half the free acid, supposing all the acid set free by the sulphuric acid to be in the alcoholic solution, was slowly added with continual stirring. The precipitate produced, which we shall call *b*, was allowed to settle, the clear solution decanted off, and the remainder of the acid therein neutralised with hot baryta-water. The precipitate produced we shall call *c*.

Precipitate *a* was dissolved in water; the solution was slightly acid. The free acid was neutralised with baryta-water, and the salt precipitated by an excess of alcohol. It was redissolved and reprecipitated several times, dried with strong alcohol, and then placed over sulphuric acid.

Precipitate *b* was slightly alkaline; the free barium oxide was neutralised with dilute sulphuric acid; when the barium sulphate subsided it was filtered out, and the organic salt precipitated from the clear filtrate by alcohol. This was redissolved, reprecipitated, solidified, and dried in the usual way.

Precipitate *c* was also slightly alkaline: it was treated in the same way as *b*.

a, *b*, and *c* were dried *in vacuo*, and until the weight became constant, in dry air at 100°, and a barium oxide determination made in each with the following results:—

a. 0·511 gram dry substance gave 0·111 gram barium sulphate = 14·27 per cent. BaO.

b. 0·463 gram dry substance gave 0·101 gram barium sulphate = 14·33 per cent. BaO.

c. 0·451 gram dry substance gave 0·106 gram barium sulphate = 15·46 per cent. BaO.

From this it is evident that the original barium salt was not a homogeneous body, but was capable of separation into at least two salts.

c was divided into three portions, after the manner in which the *a*, *b*, and *c* precipitates were obtained; they yielded—

1st portion, 15·27 per cent. BaO.
2nd „ 15·36 „ „
3rd „ 15·54 „ „

c may therefore be considered to be a homogeneous salt containing 15·5 per cent. BaO, or thereabouts.

a and *b* were mixed and then divided into three fractions after the manner described—

1st portion contained 13·59 per cent. BaO.
3rd „ „ 15·35 „ „

This latter portion is evidently the same as *c*.

The first portion was again fractionated;

the 1st fraction gave 13·23 per cent. BaO,
the 2nd „ „ 13·35 „ „
and the 3rd „ „ 14·00 „ „

It is obvious that the portion was slightly impure, and that a second definite salt was present containing 13·3 to 13·4 per cent. barium oxide. Hence, the original barium salt was capable of separation into two salts, one containing 15·5 per cent. BaO, and the other 13·3 to 13·4 per cent.

To determine whether sulphuric acid acted further on the 15·5 per cent. barium salt, 20 grams of it were dissolved in 40 c.c. water, and 2·5 c.c. sulphuric acid were diluted and added. The mixture was digested in a flask at 100° for three hours; it was not necessary to filter out the barium sulphate. At the end of three hours the acids were neutralised with baryta-water and the barium sulphate filtered out. The filtrate was evaporated to about 35 c.c., and alcohol gradually added, care being taken to avoid an excess. The precipitate was redissolved and reprecipitated eight times to insure its complete freedom from sugar, then converted into a powder (dehydrated) with absolute alcohol, and dried in a vacuum over sulphuric acid. In the absolutely dry state—dried in a current of dry air at 100°—it was found to contain 18·4 per cent. BaO. The salt was then divided into two halves by the process employed above in the case of the other salts.

The 1st part gave 18·33 per cent. BaO.
„ 2nd „ „ 18·57 „ „

We have here then another barium salt containing 18·5 per cent. or thereabouts of BaO.

The salt yielding 18·57 per cent. BaO was submitted to combustion. It was dried in a vacuum and then in dry air at 100—102° until the weight became constant.

I. 0·3552 gram dry substance, burned in a current of oxygen, gave H_2O = 0·1510 gram, CO_2 = 0·4190 gram, and $BaCO_3$ = 0·0862 gram.

II. 0·3748 gram dry substance, burned in the same way, gave H_2O = 0·1611 gram, CO_2 = 0·4426 gram, and $BaCO_3$ = 0·0888 gram.

These numbers work out,

	I.	II.	Mean.
C	33·65	33·65	33·65
H	4·72	4·77	4·74
BaO	18·84	18·43	18·63

The salt $C_{22}H_{36}O_{22}BaO$ requires—

C.....	33·69 per cent.
H	4·64 „
BaO	18·68 „

$C_{24}H_{40}O_{20}BaO$, the formula of the barium compound of a carbohydrate making the nearest approach to those numbers, requires—

C.....	35·95 per cent.
H.....	4·99 „
BaO	19·10 „

It is evident, then, that the acid is not a carbohydrate, and that the formula $C_{22}H_{38}O_{22}BaO$ is a highly probable one. It is a carbohydrate minus CH_2 plus O_2. Further investigation is required to establish definitely the constitution of this acid, but the analyses leave no doubt of the above formula.

The alcoholic solutions whence this salt was separated, were freed from alcohol by distillation, and the residue was concentrated to a syrup, which was further treated with alcohol to free it from a little barium salt. The final solution was freed from alcohol and the residue again concentrated to a syrup. On dissolving it in a little hot strong alcohol, a sugar of the $C_6H_{12}O_6$ class crystallised out. I need not describe this sugar further here than to state that it is a body crystallising in well-defined forms. Its optical activity is $[\alpha]_j = +79°$ —$+81°$ (C = 3—4) and reducing power K = 81—82°. It is enough that the presence of such a body is established, because, if I can prove that the barium salt differs from the one whence it was derived by the group $C_6H_{10}O_5$, the presence of a sugar in the alcoholic solution gives the clue to the nature of the decomposition.

A portion of the salt acted upon—the one containing 15·5 per cent. of baric oxide—was dried in the usual way and burned.

I. 0·4375 gram dry substance gave H_2O = 0·1987 gram, CO_2 = 0·5480 gram, and $BaCO_3$ = 0·086 gram.

II. 0·3823 gram dry substance gave H_2O = 0·1750 gram, CO_2 = 0·4775 gram, and $BaCO_3$ = 0·0755 gram.

	Found.		Theory for $C_{22}H_{38}O_{22}BaO$.
	I.	II.	
C	35·34	35·27	35·47
H	5·05	5·08	4·89
BaO	15·27	15·30	15·59

This demonstrates that the former salt was derived from this one in a manner represented by the equation—

$$C_{29}H_{48}O_{27}BaO + H_2O = C_{22}H_{38}O_{22}BaO + C_6H_{12}O_6.$$

The other salt, mentioned above, was found to contain—I. 13·59 per cent.; II. 13·23; and III. 13·35 BaO.

$C_{35}H_{58}O_{32}BaO$ requires 13·38 per cent. BaO.

It is obvious then that in the three salts isolated we have the series—

$C_{35}H_{58}O_{32}BaO$,
$C_{29}H_{48}O_{27}BaO$,
$C_{22}H_{38}O_{22}BaO$,

the first member of which differs from the second, and the second from the third, by the group $C_6H_{10}O_5$, and, further, this group in disuniting is hydrated to a sugar of the $C_6H_{12}O_6$ class. Now, if, as appears probable, the arabic acid molecule is broken down in the way represented, the composition of that acid could be arrived at by adding such a multiple of $C_6H_{10}O_5$ to one of the barium salts as would give a compound containing the same quantity of barium oxide as barium arabate yields.

In order to obtain evidence of other steps in the disintegration process, 200 grams of pure arabic acid, $[\alpha]_j = -27°$, were dissolved in 300 c.c. water to which 10 grams of sulphuric acid had been added, and the solution digested at 100° for an hour. The acid was then neutralised, as before, with barium hydrate, the barium sulphate filtered out, and the filtrate evaporated to 350 c.c. To this syrup alcohol was added in sufficient quantity to throw down a syrupy precipitate. This was redissolved and reprecipitated several times to free it from sugar. It was divided into three fractions in the manner described in the previous case. They were found to contain respectively—

11·24 per cent. BaO,
10·87 „ „
and 13·20 „ „

The third fraction yielded three fractions, each of which contained a quantity of BaO varying but slightly from 13·3 per cent. This is the salt $C_{35}H_{56}O_{32}BaO$, which requires 13·38 per cent. of BaO, mentioned above.

The first fraction of the original precipitate gave again three fractions containing—

11·46,
11·35,
and 11·21 per cent. BaO.

The first of these again gave three fractions containing—

11·56,
11·50,
and 11·35 per cent. BaO respectively.

The fraction containing 11·56 was dried *in vacuo* and in dry air at 100° until the weight was constant, and then submitted to combustion.

0·5324 gram dry substance gave $H_2O = 0·2490$ gram, $CO_2 = 0·7144$ gram, and $BaCO_3 = 0·0801$ gram.

	Found.	Theory for $C_{41}H_{63}O_{37}BaO$.
C.....	37·51	37·70
H	5·19	5·21
BaO	11·68	11·72

This leaves no doubt as to the nature of the body, or of the relation it holds to the other salts: the equation—

$$C_{41}H_{68}O_{37}BaO + H_2O = C_{28}H_{56}O_{32}BaO + C_6H_{12}O_6$$

shows its position.

At this stage the collateral evidence that might be afforded by the analysis of the free acid of this salt seemed to be desirable.

A known weight of the salt was dissolved in a small quantity of water, and sulphuric acid added in sufficient quantity to precipitate 98—99 per cent. of the barium. The barium sulphate was allowed to subside, and to the clear liquid strong alcohol was added until a considerable precipitate was formed. When the supernatant liquid became clear, it was carefully decanted off, and poured slowly with continual stirring into an excess of absolute alcohol. The resulting white flocculent precipitate, when washed with absolute alcohol, pressed as free as possible from that liquid, and dried over sulphuric acid, was very nearly free from ash. It was dried *in vacuo* and finally in dry air at 100° for analysis.

I. 0·3255 gram dry substance gave H_2O = 0·1770 gram, CO_2 = 0·4990 gram, ash = 0·0045 gram.

II. 0·2950 gram dry substance gave H_2O = 0·1550 gram, CO_2 = 0·4550 gram, ash = 0·0035 gram.

	Found.		Theory for $C_{41}H_{68}O_{37}$.	Theory for $C_{41}H_{66}O_{36}$.
	I.	II.		
C	42·36	42·57	42·71	43·38
H	6·12	5·90	5·90	5·82

The ash is allowed for in the calculations.

The acid was again dissolved in a little water, strong alcohol added to produce a slight precipitate, which was allowed to subside, and the clear supernatant liquid slowly poured, as before, into absolute alcohol. The white flocculent precipitate was dried as usual. It was free from ash.

I. 0·2925 gram of dry substance gave H_2O = 0·1605 gram, CO_2 = 0·4610 gram, no ash.

II. 0·3148 gram gave H_2O = 0·1727 gram, CO_2 = 0·4956 gram, no ash.

These numbers yield the following percentages:—

	Found. I.	Found. II.	Theory for $C_{41}H_{68}O_{37}$.	Theory for $C_{41}H_{66}O_{36}$.
C	42·98	42·94	42·71	43·38
H	6·10	6·10	5·90	5·82

0·732 gram dry acid dissolved in water and exactly neutralised with clear baric hydrate, yielded 0·146 gram baric sulphate.

	Found.	Theory for $C_{41}H_{68}O_{37}BaO$.
BaO	11·59	11·71

The aqueous solution of the acid is without action on polarised light. A solution containing in 100 c.c. at 15·5° 4·290 grams dry acid gave sp. gr. = 1·01725. Calculating from this, the gravity of a solution of 1 gram in 100 c.c. is 1·00402, a higher number than is yielded by any known carbohydrate. Its aqueous solution reduces cupric oxide slowly, the K after long boiling being 28·5.

Thus far the composition of the four acids and their relation one to the other may, I think, for the purpose of this investigation, in its present stage at least, be looked upon as satisfactorily established. To go a step further, I proceeded in another way.

As pointed out above, barium arabate gave 6·00 per cent. of barium oxide, whilst the last salt described contained 11·71 per cent. Now, as the four salts isolated were shown to differ one from the other by $C_6H_{10}O_5$, it is obvious that if arabic acid differs from the acid last examined in the same way as this differs from those below it, there must be many acids between the two. Some of these bodies I have prepared, and shall refer to them later on, but as their percentage of carbon and hydrogen closely approaches that of a carbohydrate, their analysis, for the present, is of no advantage. If I can prove that arabic acid yields $C_{41}H_{68}O_{37}$, and, at the same time, either a sugar or sugars or some such carbohydrate, there will be no difficulty, with the facts already established, in arriving at the composition of that acid.

The alcoholic supernatant liquid from which the salt $C_{29}H_{48}O_{27}BaO$ was separated, was freed from alcohol by distillation, and the residual syrup concentrated and treated with an excess of boiling alcohol, sp. gr. 0·83, to separate a little barium salt retained by the first alcohol. This process was repeated until the residual syrup was free from all trace of barium salt. It was then treated with a little animal charcoal, concentrated, and dissolved in the least possible quantity of boiling strong alcohol.

The syrup contained solid matter, of which the optical activity was

$[\alpha]_j = + 86{\cdot}0°$ (C = 5·5 grams), and cupric reducing power K = 95—96.

The alcoholic solution on standing a few days began to deposit crystalline crusts, which rapidly increased in quantity. These were separated from the liquid; they were anhydrous. The optical activity of the body was

$$[\alpha]_j = + 93{\cdot}8° \text{ (C = 4·5)},$$

and the cupric reducing power, K = 103.

This sugar was dissolved in a little water, and strong alcohol added in small quantity. After standing a short time a crop of warty crystals appeared, which increased very little after the first few days. The radiations from the warty masses were well-defined glassy rhombic prisms with wedge-shaped terminations (rhombic prism terminated by a macrodome), corresponding exactly with the description of arabinose given by Scheibler (*Ber.*, **6**, 612). He states, however, that the optical activity of the sugar is $[\alpha]_j = + 151°$ — $+ 121°$, with K indefinite but inclined to something above 100. I determined these factors for my preparation, and found them to be—

$$[\alpha]_j = + 91° \text{ (C = 3·55)}$$
$$K = 99{\cdot}4—100.$$

A second and a third crystallisation gave practically the same results; hence, the original crystals must have contained, besides this sugar, a small quantity of a higher rotating sugar with a K greater than 100, and there must also be some error in Scheibler's description.

As I had the pure body in my hands, I burned it. The crystals lose nothing in dry air at 100°.

0·334 gram dry substance gave $H_2O = 0{\cdot}204$, $CO_2 = 0{\cdot}491$, ash free.

	Found.	Theory for $C_6H_{12}O_6$.
C	40·09	40·00
H	6·78	6·67

Kiliani (*Ber.*, **13**, 2304) gives the optical activity of arabinose, $[\alpha]_D = +79{\cdot}0°$ (C = 4·62); my number, calculated after him, is $[\alpha]_D = +80{\cdot}4°$ (C = 3·56). There is a considerable variation in apparent specific rotatory power with the concentration, and a freshly-prepared solution possesses an opticity 1·6—1·7 times greater than a solution of the same strength that had been boiled for some time, or after standing 24 hours. But upon these matters we need not dwell at present. I have established that we have to do with a distinct and definite sugar of the $C_6H_{12}O_6$ class, which, for reasons to be made obvious later on, I propose to call *γ-arabinose*. I have the pure body,

in quantity, in my hands; more detailed description of it belongs to another place.

The alcoholic mother-liquid whence γ-arabinose crystallised, was freed from alcohol by distillation, and the residue evaporated to a thick syrup. To this, strong alcohol was added until a syrupy precipitate began to form; it was then put aside. At the end of a week the liquid was thick with crystals, which were filtered out and washed with alcohol. They were found to have an apparent sp. rot. pr., $[\alpha]_j = +101°$ (C = 3·58), and a reducing power, K = 105. Here, then, we have a body distinctly different from γ-arabinose; it has to be determined whether it is a simple body or a mixture.

80 grams of it were dissolved in as little water as possible, and alcohol, 0·83, added until a syrupy precipitate began to form, care being taken to suspend the addition of alcohol immediately the precipitate showed itself, and then a few drops of water added to redissolve any that had formed. At the end of eight days the liquid was full of crystals; they were filtered out and washed with alcohol, so gauged in strength as not to produce a precipitate in the mother-liquid. This latter was kept separate from the washings. The crystals, when dry, weighed 18 grams. The apparent sp. rot. pr., after boiling, was found to be,

$$[\alpha]_j = +\ 111{\cdot}1\ (C = 3{\cdot}562),$$

and the reducing power, K = 110. The optical activity of the freshly prepared solution—the temporary activity—was 1·5 to 1·6 times greater than the permanent one given above.

The 18 grams were divided into three parts by fractional crystallisation. Each fraction gave practically the same opticity and K as was given by the original substance. The crystals were anhydrous; and, as the substance was a pure body, I submitted it to combustion.

0·326 gram of dry substance gave H_2O = 0·195 gram, CO_2 = 0·4775 gram, no ash.

	Found.	Theory for $C_6H_{12}O_6$.
C	39·94	40·00
H	6·63	6·67

These numbers leave no doubt as to the composition of the body. This sugar I shall call *β-arabinose*.

It appears to me almost certain that it was of this sugar, in an impure state, that Scheibler, when describing his arabinose, determined the optical activity, $[\alpha]_j = +115° - +121°$, while he determined the crystalline form of γ-arabinose described above. The crystals of β-arabinose are not rhombic; the prisms are no doubt rhombic in appearance, but the terminations are decidedly monoclinic.

Claëson (*Ber.*, **14**, 1271) also, no doubt, had this sugar in an impure state in his hands, for he takes Kiliani back again to Scheibler's sugar, $[\alpha]_j = +115° - +121°$, by ascribing to arabinose the optical activity, $[\alpha]_D = +109{\cdot}9$ ($[\alpha]_j = +122°$). I shall be able to show that this high opticity is due to an admixture with β-arabinose of a third sugar of higher opticity, which shall be known as *α-arabinose*.

Kiliani (*Ber.*, **15**, 34) admits that there is a sugar of the high opticity stated by Claëson, and agrees with him that one gum may yield the one sugar and another the other. We now see some of the difficulties of these investigators; not one but three sugars were being dealt with, and they are produced side by side.

It is sufficient for my present purpose that I have proved the presence of a second distinct $C_6H_{12}O_6$ sugar.

The 80 grams of substance employed above were no doubt a mixture of at least two bodies; β-arabinose, and another of lower opticity and reducing power, probably γ-arabinose. If this be so, it should be possible to separate the second sugar from the mother-liquid. The second fraction from this liquid had a sp. rot. pr., $[\alpha]_j = +101°$, and the third, $[\alpha]_j = +95{\cdot}8°$. The residue, when syruped and dissolved in strong alcohol, gave a crop of crystals, of which the opticity and reducing power were found to be

$$[\alpha]_j = +90{\cdot}8° \text{ and } K = 100{\cdot}5.$$

Hence, it is the rhombic arabinose, γ-arabinose, above mentioned. The 80 grams were then, undoubtedly, a mixture of the two sugars, β- and γ-arabinose. If we now turn to the syrup whence these two sugars were derived, compare its factors,

$$[\alpha]_j = +86{\cdot}0° \text{ and } K = 95—96,$$

with those possessed by them, and consider that they were separated from it, it will be obvious that at least a third sugar, of lower optical activity than either of them, must be present. The mother-liquid from the 80 grams crystals, dealt with above, yielded such a sugar; it is a $C_6H_{12}O_6$ body, with an apparent sp. rot. pr.,

$$[\alpha]_j = +79° — +81°,$$

and cupric reducing power probably not greater than K, = 81—82. It shall be known as *δ-arabinose*. I need not describe it further here. The factors of the mother-liquid of this sugar point distinctly to a fourth sugar, but I have not yet succeeded in crystallising it; it has a lower opticity than δ-arabinose, and is, no doubt, also a $C_6H_{12}O_6$ body.

I need not go further with the constitution of this syrup: there can be no doubt, from the way in which the sugars crystallised from it,

that it is composed of $C_6H_{12}O_6$ bodies. We have then, when arabic acid is split up, on the one hand, the acid, $C_{29}H_{48}O_{27}$, and on the other four, probably five sugars, some of which are well defined $C_6H_{12}O_6$ bodies, and further, when the acid $C_{29}H_{48}O_{27}$ is converted into $C_{23}H_{38}O_{22}$, we have a single sugar produced, which is easily crystallisable and identical with δ-arabinose, the equation,

$$C_{29}H_{48}O_{27} + H_2O = C_{23}H_{38}O_{22} + \underset{\delta\text{-Arabinose.}}{C_6H_{12}O_6},$$

representing the change. These facts lead us irresistibly to the conclusion that arabic acid is converted into $C_{29}H_{48}O_{27}$ by the splitting-out with hydration, of at least four, probably five or more $C_6H_{10}O_5$ molecules.

I have shown that the barium arabate with which I worked contained 6·00 per cent. barium oxide. Free arabic acid, dried in dry air at 100°, yielded, on combustion in oxygen, the following results:—

	I.	II.	III.	IV.	V.	VI.
C....	44·53	44·45	44·73	44·36	44·37	44·48
H ..	6·17	6·13	6·13	6·09	6·07	6·07

The numbers I, III, V, and VI were obtained respectively from the above-mentioned precipitates 1, 2, 3, and 4, into which arabic acid was divided.

These numbers agree exactly with Mulder's results, but they differ materially from those given by Scheibler and others. Scheibler's numbers lead to the formula

$$C_{12}H_{22}O_{11},$$

mine to $C_6H_{10}O_5$

which requires C = 44·44

H = 6·17;

but it is obvious that no multiple of $C_6H_{10}O_5$ can have the same formula as a multiple of that group plus one of the acids, the composition of which I have satisfactorily determined. Now, bearing in mind that barium arabinate contains 6·0 per cent. BaO, and that the acids are derived from arabic acid by the elimination of multiples of the $C_6H_{10}O_5$ group, it is clear that the formula of arabic acid must be the formula of one of the acids plus such a multiple of $C_6H_{10}O_5$ as will yield a barium salt containing 6·0 per cent. BaO.

$$C_{41}H_{68}O_{37} + 8C_6H_{10}O_5 = C_{89}H_{148}O_{77}$$

requires

C = 43·58

H = 6·04

numbers which do not agree satisfactorily with the analytical figures; but if we take

$$C_{41}H_{68}O_{37} + 8C_6H_{10}O_5 = \underset{\text{Arabic acid.}}{C_{89}H_{142}O_{74}} + 3H_2O,$$

we get a formula which requires

$$C = 44{\cdot}61$$
$$H = 5{\cdot}93,$$

numbers agreeing exactly with the combustion percentages, and the barium salt, $C_{89}H_{142}O_{74}BaO$, requires 6·00 per cent. BaO, the amount found being—

I, 6·10; II, 5·90; III, 6·00; and IV, 6·06.

Calcium salts were prepared in the same way as the barium ones, by neutralising solutions of precipitates 1, 2, and 3 with clear lime-water, and precipitating with alcohol. The three salts were dried as usual and burned in a current of oxygen, with the following results:—

	Found.			Theory for $C_{89}H_{142}O_{74}CaO$.
	I.	II.	III.	
C.....	43·24	43·29	43·29	43·59
H	6·08	5·97	5·92	5·79
CaO ..	2·30	2·38	2·39	2·28

These numbers, with the facts already established, prove, as far as it can be proved, that arabic acid is represented by the formula $C_{89}H_{142}O_{74}$.

Between this acid and the acid, $C_{41}H_{68}O_{37}$, therefore, eight $C_6H_{10}O_5$ molecules must be thrown out and eleven molecules of water taken up, three by the acids, and eight by the carbohydrates. For the present, I do not think it necessary to bring forward evidence of the taking up of the three water-molecules by the acids. It must suffice if I can produce further evidence to show that arabic acid is gradually converted into lower acids with the elimination of $C_6H_{10}O_5$, and the formation of sugars of the $C_6H_{12}O_6$ class.

60 grams of pure arabic acid were dissolved to 200 c.c. solution in water containing 4 grams of sulphuric acid, and digested 15 minutes at 100°. At the end of that time the acid was neutralised with hot barium hydrate solution, and, as it was impossible to separate the barium sulphate from the barium salts of the higher acids by filtration, the barium sulphate passing through even three or four filter-papers, alcohol was added as long as a precipitate formed. The clear supernatant liquid was freed from alcohol by distillation, and the concentrated syrup by a second treatment with alcohol from barium

salt. The syrup from the third treatment contained solid matter, of which the opticity was

$$[\alpha]_j = + 128°,$$

a number much higher than that yielded by β-arabinose. To this syrup strong alcohol was added until a syrupy precipitate began to appear. On heating, this redissolved, and, as the solution cooled, crystals began to form. At the end of 24 hours they completely filled the liquid. These crystals gave the following factors:—

$$[\alpha]_j = + 119°$$
$$K = 103—105°$$

They were again dissolved and allowed to crystallise; the first fraction was found to have an opticity,

$$[\alpha]_j = + 111{\cdot}5°,$$

and cupric reducing power, K = 110.

These are the factors of β-arabinose. The crystals obtained from water showed, too, the same characteristic monoclinic terminations as that body.

The mother-liquid contained another sugar, *α-arabinose*, the optical activity of which must be well above $[\alpha]_j = + 140°$. I cannot describe this body more particularly at present; it is sufficient that, amongst the products of this decomposition, neither γ- nor δ-arabinose is present, nor are any of the lower rotatory sugars to be found. Let us examine the nature of the other bodies produced at the same time.

The precipitate insoluble in alcohol was dissolved in water, the barium sulphate remaining suspended, and alcohol, in small quantities at a time, added until the solution began to break. By precipitating a little of the organic baric salt in this way, the whole of the barium sulphate is taken down with it. The solid matter in the supernatant liquid was divided into three parts by fractional precipitation with alcohol. The first and third fractions were further purified by being several times redissolved and reprecipitated.

The first fraction was dried as usual and the barium oxide determined.

0·713 gram dry substance gave 0·07 gram $BaSO_4$.

	Found.	Theory for $C_{83}H_{132}O_{69}BaO$.
BaO.....	6·45	6·41

The third fraction was treated in the same way.

0·705 gram dry substance gave 0·079 gram $BaSO_4$.

	Found.	Theory for $C_{71}H_{112}O_{59}BaO$.
BaO.....	7·36	7·42

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Hence, besides the two sugars, acids differing from arabic acid by $C_6H_{10}O_5$ molecules, are produced, the following equations representing the change:—

I.... $C_{89}H_{142}O_{74} + H_2O = C_{83}H_{132}O_{69} + C_6H_{12}O_6$.
Arabic acid. α-Arabinosic acid. α-Arabinose.

II.... $C_{83}H_{132}O_{69} + H_2O = C_{77}H_{122}O_{64} + C_6H_{12}O_6$.
β-Arabinosic acid. α- or β-arabinose.

III.... $C_{77}H_{122}O_{64} + H_2O = C_{71}H_{112}O_{59} + C_6H_{12}O_6$.
γ-Arabinosic acid. β-Arabinose.

As some of the further steps in the process of breaking down have not been followed, we arrive at the next products examined by the following equation, which unites six steps:—

III, IV, V, VI, VII, and VIII } $C_{77}H_{122}O_{64} + 9H_2O = C_{41}H_{68}O_{37} + 6C_6H_{12}O_6$.
θ-Arabinosic acid. β-, γ-, δ- and other arabinoses in undetermined quantities.

Between this acid, θ-arabinosic, and the acid, $C_{29}H_{48}O_{27}$, I have not determined the sugar or sugars thrown out; but between the latter body and $C_{23}H_{38}O_{22}$ only one sugar, δ-arabinose, is produced, one $C_6H_{10}O_5$ molecule being hydrated.

IX..... $C_{41}H_{68}O_{37} + H_2O = C_{35}H_{58}O_{32} + C_6H_{12}O_6$.
ι-Arabinosic acid. δ-Arabinose (?)

X..... $C_{29}H_{48}O_{32} + H_2O = C_{29}H_{48}O_{27} + C_6H_{12}O_6$.
κ-Arabinosic acid. δ-Arabinose (?)

XI..... $C_{29}H_{48}O_{27} + H_2O = C_{23}H_{38}O_{22} + C_6H_{12}O_6$.
λ-Arabinosic acid. δ-Arabinose.

This last arabinosic acid is a very stable body, resisting the action of a 3 or 4 per cent. solution of sulphuric acid for many hours.

It will be interesting to follow this last acid further. From the evidence to hand I am inclined to think that it no longer behaves like its predecessors, but is broken down in a more complicated way. There is no necessity, however, at present to take the matter further. I have conclusively demonstrated, in a broad way, the constitution of arabic acid, and characterized, sufficiently for my purpose, its decom-

position-products. I have not described the bodies as fully as I should wish, but if I were to describe them with any degree of minuteness, more time and space would be occupied than are necessary for the immediate object of this work. Descriptions of the various sugars, as well as of the different *arabinosic acids* (in contradistinction to arabic acid) will more suitably form subjects for future separate communications.

Before concluding this part of the work, I may state that arabic acid [$[\alpha]_j = -27° - -28°$ (C = 4 to 5)] is the chief constituent of all the lævorotatory gums examined by me, and I carefully examined Levantine, Senari, East Indian, and Senegal gums; but other acids are also, at times, present which hold, I believe, a very simple relation to arabic acid. I have separated fractions from some of these gums, of which the optical activity varied between $[\alpha]_j = -22°$ and $[\alpha]_j = -34°$. This variation in optical activity is attended with a variation in the percentage of barium in the barium salts, the low rotating fractions containing 6·5—6·7 per cent. barium oxide; the barium salt of α-arabinosic acid, $C_{83}H_{132}O_{69}BaO$, mentioned above, requires 6·41 per cent. BaO. The high rotating fractions give 5·6—5·8 per cent. BaO in their barium salts: hence they contain acids of a larger molecule than arabic acid; $C_{95}H_{152}O_{80}BaO$, containing a $C_6H_{10}O_5$ molecule more than arabic acid, requires 5·8 per cent. BaO.

In the next part I shall describe the dextrorotatory gums, of which Gedda gum is a type, and I probably shall have to devote a part to the optically inactive gums, of which we have an example in Australian gum; but I may say here that the acids of these gums are built up after the same manner as arabic acid.

VIII.—*On the Preparation of Pure Chlorophyll.*

By Dr. A. Tschirch.

All attempts hitherto made to prepare pure chlorophyll must be regarded as failures, their authors having started with the idea that chlorophyll is a comparatively stable substance, not altered by treatment with hydrochloric acid, &c. But an exact study of the alterations produced in the very characteristic spectrum of living leaves and of alcoholic chlorophyll-solutions, by the action of various reagents, shows that pure chlorophyll is an extremely unstable body, which is decomposed even on treating the leaves with alcohol, even though no

alteration of colour is thereby produced. Hence it follows that the substances hitherto described as "chlorophyll" or "crystallised chlorophyll," and obtained either by treating chlorophyll extracts with strong hydrochloric acid, and precipitating the resulting blue solution (phyllocyanin) with excess of water* or with marble†—*i.e.*, by energetic chemical actions—or by absorbing the chlorophyll from its alcoholic solution with animal charcoal and washing it out with ether‡—must be regarded as products of decomposition more or less remote from the original substance.

This conclusion is confirmed by spectroscopic examination, which shows that the crystallised chlorophyll of Gautier and Rogalski is identical with the chlorophyllan of Hoppe-Seyler (*Zeitschr. Physiol. Chem.*, **3**, 347), which, as I have shown (*Ber. der deutsch. botan. Gesellsch.* **1**, 145), is a product of the oxidation of chlorophyll, and that the pure chlorophyll of Berzelius, Mulder, and Pfaundler is identical with Frémy's phyllocyanic acid.§ Here then are two bodies which agree perfectly in their absorption-spectra, but—as shown by their behaviour to caustic alkalis, which dissolve phyllocyanic acid, but not chlorophyllan—are nevertheless totally distinct one from the other.‖

But it is not only towards concentrated acids that chlorophyll is so sensitive, for it is quickly decomposed even by weak acids,¶ always with formation of chlorophyllan. The constant presence of vegetable acids in the cells of the leaf explains therefore the rapid decomposition of chlorophyll-tinctures, which, as may be shown spectroscopically, takes place even during the preparation of the solution, and goes on till the whole of the chlorophyll is converted into chlorophyllan, as evidenced by the change of colour of the liquid from green to yellow. Hence all attempts to obtain the colouring-matter in the pure state from chlorophyll solutions, either by precipitation with saline solutions, as I formerly proposed (*loc. cit.*, p. 181), or by

* Berzelius (*Annalen*, **27**, 298).—Harting (*Pogg. Ann.*, **96**, 547).—Pfaundler (*Annalen*, **115**, 43).

† Mulder (*J. pr. Chem.*, **33**, 479).

‡ Gautier (*Compt. rend.*, **89**, 862).—Rogalski (*Compt. rend.*, **90**, 881), and Rôle de la chlorophylle dans l'assimilation.—*Inauguraldissertation*, Krakau.

§ (*Compt. rend.*, **61**, 191.)—I here designated as *Phyllocyanic acid* only the body formed by decomposition of phyllocyanin, which is not identical with that which Frémy obtained by treating chlorophyll with barium hydroxide, magnesia, or alumina, and decomposing the resulting salts with acids.

‖ The spectroscopic behaviour of these two bodies shows therefore that a body may undergo chemical alterations not recognisable by spectroscopic observation.

¶ Compare also Kraus, "Zur Kenntniss der Chlorophyllfarbstoffe und ihrer Verwandten."—Stuttgart, 1872. Sachsse, "Die Farbstoffe, Kohlehydrate und Proteinsubstanzen."—Leipzig, 1877.

separation with benzene, carbon sulphide, &c., fail in their object, inasmuch as the colouring-matter is decomposed by the accompanying substances, even during the process of extracting it from the leaves.

Equally unavailing have been the attempts made to prepare the pure colouring-matter by saponification of chlorophyll extracts. Chautard (*Compt. rend.*, **76**, 570) has drawn attention to the differences between the spectroscopic characters of these alkaline solutions of chlorophyll and those of chlorophyll tincture. I myself have also further studied the action of alkalis, and have found that this treatment always yields products of decomposition, recognisable as such by their spectroscopic characters.

According to the present state of our knowledge, we must regard as pure chlorophyll the product whose absorption-spectrum agrees with that of living leaves, as regards both the positions of the individual bands and likewise their breadth and intensity. Such a body I have obtained by reduction of chlorophyllan, a substance easily obtained in the crystalline state by the action of zinc-dust on alcoholic solution of chlorophyllan at the heat of the water-bath. The alcoholic solution of this splendid emerald-green body exhibits the following absorption-spectrum:—

Band.	I.	II.	III.
Thin layers	λ = 68—63	62—59·5	58·3—55·7
Thick layers	λ = 68·5	55·5	

Band.	IV.	End-absorption.
Thin layers ..	λ = 54·0—52·5	50 to the end*
Thick layers..	λ = 53·5—52	51 to the end

The absorption-spectrum of living leaves exhibits the following bands:—

Band.	I.	II.	III.
2 Leaves.....	λ = 70—65	63—61	60—57
3 Leaves.....	λ = 70·5	57	

Band.	IV.	End-absorption.
2 Leaves..	λ = 55—54	52 to the end†
3 Leaves..	λ = 55—54	52 to the end

Disregarding the shifting of all the bands towards the red, which is apparent in the spectrum of living leaves, and, according to Kundt (*Pogg. Ann.*, 1874, *Jubelband*, 615), is due to the shifting influence of

* The measurements are made, according to Ångström's scale, in wave-lengths of $\frac{1}{100000}$ mm.

† The sun-light employed was highly concentrated by a large double convex lens, the invisible heat-rays being intercepted by three alum cells.

the solvent, or of accompanying substances in the grain of chlorophyll, the bands of the two spectra agree perfectly in breadth and intensity. The order of intensity of these bands, starting from the darkest, is in both spectra—

I II III IV.

Especially characteristic are the relative breadth and darkness of III, which in the chlorophyll solutions always appears narrower;* also the remarkable narrowness and brilliancy of IV:† even in very thick layers, by which the bands I—III are fused into a single broad band, band IV is in both cases still dull and indistinct.

In the end-absorption, the pure chlorophyll prepared by reduction of chlorophyllan does not show any perceptible bands. On diluting the solution, or diminishing the thickness of the layer traversed by the light, the end-absorption gradually recedes towards the blue. The band between *b* and F observed in the living leaf belongs to the accompanying yellow colouring matters.

Pure chlorophyll prepared as above forms blackish-green drops, which have not yet been made to crystallise. It dissolves with great facility in alcohol, ether, and benzene, easily also in oils both fatty and volatile, sparingly in fused paraffin, not at all in water. It is converted by dilute acids into yellow chlorophyllan, by strong hydrochloric acid into blue phyllocyanin, and is resolved by potash-lye into an emerald-green substance which dissolves readily in water, forming an emerald-green strongly fluorescing liquid, externally very much like chlorophyll solutions, and a yellow body which may be extracted by ether from the aqueous solution. The alcoholic solution of pure chlorophyll is much less sensitive to light than ordinary tincture of chlorophyll. I regard this pure chlorophyll as identical with the chlorophyll of living plants, and reserve to myself the right of examining it further.

The following is a contribution to the synonymy of certain bodies of the chlorophyll-group:—

Chlorophyll (Pelletier and Handbooks) = crude chlorophyll (Wiesner).
Cyanophyll + Xanthophyll (G. Kraus).

Cyanophyll (G. Kraus) = chlorophyll (Wiesner).
Blue chlorophyll (Sorby).
Pure chlorophyll (Tschirch) + some α-Xanthophyll.

* Compare the representation of the chlorophyll spectrum by Pringsheim (*Berlin Akad. Monatsberichte*, 1874, October), to whom we are indebted for the latest exact representation of the spectrum.

† In the solutions band IV is relatively dark (*vide* Kraus, Hagenbach, &c.).

Chlorophyllan (Hoppe-Seyler) = Modified chlorophyll (Stokes).
Acid chlorophyll of the Handbooks.
Acidoxanthin (C. Kraus).
Filhol's precipitate (obtained on adding organic acids to chlorophyll tincture).
Crystallised chlorophyll (Gautier and Rogalski).
Pure chlorophyll (Jaudin).
Yellow chlorophyll (Sorby).
α-Hypochlorin (Pringsheim's hypochlorin).
(?) Borodin's chlorophyll crystals.
Colouring-matter which produces the winter fading of certain evergreen plants (Haberlandt, G. Kraus, Askenasy).
Colouring-matter which produces the discoloration of strongly acid leaves in the dark.

Phylloxanthin (Frémy?) (Tschirch) = xanthophyll (Berzelius) ex part.
? Chlorophyllic acid (Liebermann).
Xanthin (C. Kraus).

Phylloxantheïn (Weiss) = alkali phyllocyanate (Tschirch).
Frémy's etiolin.

Phyllocyanic acid (Frémy, ex part) = pure chlorophyll (Berzelius, Mulder, Pfaundler, Harting).

Body precipitated by water from solution of phyllocyanin (Tschirch).
(?) Chlorophyllanic acid (Hoppe-Seyler).

Potassium chlorophyllinate (Tschirch) = Chlorinkali (C. Kraus).
Sachsse's precipitate formed by potassium or sodium in solution of cyanophyll.

α-Xanthophyll* = xanthophyll (G. Kraus).

β-Xanthophyll = xanthophyll (Pringsheim). Yellow colouring-matter of autumn leaves (perhaps identical with α).

γ-Xanthophyll = yellow colouring-matter soluble in ether; precipitated by potash from cyanophyll.
Xanthin (Dippel).
Xanthin (C. Kraus) ex part.

δ-Xanthophyll = Frémy's phylloxanthin, separated by barium hydroxide from cyanophyll.

ε-Xanthophyll = yellow colouring-matter formed in Sachsse's reaction (treatment of cyanophyll solution with sodium); permanent in benzene solution (perhaps identical with γ).

* The xanthophylls here enumerated are perhaps identical; but till the point is definitely established, they may be conveniently distinguished by Greek letters.

Xanthophyll (G. Kraus) = etiolin (G. Kraus).
Xanthophyll (Sorby) ex part.
Erythrophyll (Bougarel ?) = chrysophyll (Hartsen).
Borodin's yellow crystals.
ε-Xanthophyll (Tschirch).
Anthoxanthin (Marquardt) = anthoxanthin (Pringsheim).
Xanthin and Xantheïn (Frémy and Cloëz).
Yellow colouring-matters of flowers.

IX.—*The Halogen Compounds of Selenium.*

By Franklin P. Evans, Associate of University College, Bristol, and William Ramsay, Ph.D.

The experiments to be described were undertaken in order to compare the stability of the halogen compounds of selenium with those of sulphur, by measuring their amount of dissociation caused by rise of temperature.

Of the three chlorides of sulphur which are known, the monochloride is the only one stable at the ordinary temperature. The dichloride appears to be capable of existence at temperatures not exceeding 120—130°, but even at 20° dissociation has already begun; and the liquid prepared by saturating sulphur monochloride (S_2Cl_2) with chlorine at that temperature contains, according to Michaelis (*Annalen*, **170**, 1), only 93·45 per cent. of the dichloride SCl_2, the remainder consisting of monochloride. At still lower temperatures the tetrachloride is capable of existence; and at − 22° a saturated solution of chlorine in S_2Cl_2 is found to contain chlorine corresponding to the formula SCl_4.

The dichloride of selenium, on the other hand, appears to be incapable of existence. When chlorine is passed over selenium, the monochloride is first formed, but excess of chlorine converts it into the stable tetrachloride. The action of heat on these compounds has, so far as we know, not been studied, and we have the honour of bringing before the Society the results of our experiments to ascertain the effects of that action.

After the monochloride had been prepared by the usual method, an attempt was made to distil it, excess of selenium being present, so as to ensure absence of tetrachloride. The liquid began to boil at 145°, and as it passed over, the temperature gradually rose to 175°;

the residue in the bulb consisted of selenium, together with some monochloride. The residue in the bulb was again treated with chlorine, selenium being again purposely left in excess; and on again distilling, the first portions of liquid passed over at 124°, and towards the end of the distillation the temperature again rose to about 180°. The distillate deposited crystals which were found to consist of the tetrachloride. It was placed in a clean bulb, and a large excess of powdered selenium was added; however, on again distilling, the same results were obtained; the monochloride passed over, partially dissociating into tetrachloride, and free selenium, which remained in the bulb.

These experiments show that selenium monochloride has no constant boiling point, but splits up on application of heat into selenium and the tetrachloride. It is possible, however, to free the monochloride from tetrachloride by addition of carbon disulphide. The former mixes easily, while the latter is deposited, for it is nearly insoluble in carbon disulphide. The mixture of monochloride and carbon disulphide was decanted from the tetrachloride, placed in a fractionating bulb, and heated over a water-bath. The distillate was at first nearly colourless, but gradually assumed a darker colour owing to volatilisation of monochloride together with bisulphide. When the temperature had reached 57° ebullition stopped. The distillate was collected in three portions; the first consisted of faintly tinged carbon disulphide; the second and third were more deeply coloured, and contained a crystalline deposit of the tetrachloride. Analyses were made of the liquid portions, with the following results:—

Fraction 2.

AgCl 0·384 gram equivalent to chlorine	0·0949
Se	0·1560

Percentage composition:—Se = 62·17; Cl = 37·83.

Fraction 3.

AgCl 1·2780 grams equivalent to chlorine	0·3158
Se	0·5480

Percentage composition:—Se = 63·43; Cl = 36·57.

These analyses show merely the proportion of selenium to chlorine, the carbon disulphide being neglected.

As the percentage composition of Se_2Cl_2 is Se = 69·14, Cl = 30·86 per cent., and that of $SeCl_4$ is Se = 35·90, Cl = 64·10 per cent., it is evident that the distillates consisted of a mixture of monochloride and tetrachloride, and as the proportion of chlorine in fraction No. 2 is greater than that in fraction No. 3, more decomposition has ensued

at the beginning of distillation than at the end; and it appears probable that the presence of the element selenium in the bulb tends to arrest the dissociation of monochloride into tetrachloride.

The residue in the bulb was nearly free from carbon disulphide, the mean result of four concordant analyses being Se = 65·02, Cl = 29·58, = 94·60 per cent. The difference between this number and 100 = 5·40 per cent., is to be attributed to the presence of carbon disulphide. The ratio between selenium and chlorine expressed centesimally is Se 69·78 : Cl 30·22, and the substance therefore nearly corresponds to the formula Se_2Cl_2.

The liquid therefore consisted of—

Se_2Cl_2.....	94·60 per cent.
CS_2.....	5·40 ,,
	100·00

The vapour-density of this mixture, which was the nearest approach to pure monochloride which we could obtain, was determined by Victor Meyer's process at temperatures between 200° and 250°.

1. Amount taken, 0·1550 gram. Air collected, 16·6 c.c. Temperature, 5·0°. Pressure, 748·5 mm. Vapour-density, 107·75.
2. Amount taken, 0·1135 gram. Air collected, 11·2 c.c. Temperature, 8·0°. Pressure, 745·5 mm. Vapour-density, 118·68.
3. Amount taken, 0·1700 gram. Air collected, 17·0 c.c. Temperature, 11·5°. Pressure, 753·2 mm. Vapour-density, 117·36.

Mean of three determinations, 114·59.

Theoretical vapour-density of above mixture, 110·80.

From these numbers it would appear either that selenium monochloride does not split up on heating, or that if it does the products are selenium and chlorine, for we have observed no indication of the existence of a dichloride. In the latter case the following reaction would occur, and it is to be remarked that it would not necessitate any change in volume.

$$Se_2Cl_2 = Se_2 + Cl_2.$$
$$2 \text{ vols.} \quad — \quad 2 \text{ vols.}$$

We believe that this equation represents what really occurs, as we shall show hereafter. A third reaction is possible, but it would necessitate a vapour-density apparently much higher than that found. It is—

$$2Se_2Cl_2 = SeCl_4 + 3Se.$$
$$4 \text{ vols.} \quad 2 \text{ vols.} \quad —$$

It is possible that this reaction takes place partially, for it has been

pointed out that when the monochloride is distilled, the tetrachloride volatilises, and selenium is set free.

The action of heat on the tetrachloride was next studied. This substance was prepared in the pure state by washing the product of the action of chlorine on the monochloride with carbon disulphide to remove the monochloride. The carbon disulphide was expelled by heating the residue gently in a current of dry air. The substance obtained was found to have the following composition:—

Taken 0·5620 gram.

AgCl found 1·471 gram	= chlorine	0·3636 gram.
Se „		0·1910 „

Percentage composition:—

	Found.	Calculated.
Selenium.....	33·99	35·90
Chlorine	64·69	64·10

This preparation consisted of light yellow crystals, and was evidently pure. It was analysed by boiling with sulphurous acid, and collecting the precipitated selenium on a weighed filter, a method which does not give very accurate results, but was the only one at our disposal. The vapour-density of the tetrachloride was determined at various temperatures with the following results:—

Temp.	Amount taken.	c.c. of air collected.	T. of atmosphere.	P. of atmosphere.	Vapour-density.
180°	0·1360 gram	14·40	12°	756	110·25
200	0·1490 „	15·85	15·5	754	111·76
200	0·1425 „	15·05	16·0	757·7	112·36
210	0·1128 „	14·40	15·0	760	92·23
225	0·1182 „	16·70	18·0	760	84·20
245	0·1063 „	15·70	15·0	760	79·72
295	0·1040 „	16·65	11·3	757·7	72·82
350	0·1055 „	18·63	12·3	755·0	66·49

The theoretical vapour-density of selenium tetrachloride is 110·2. It is evident, therefore, that at temperatures below 200° the vapour-density is normal, and decomposition has not taken place. At higher temperatures, however, it proceeds very rapidly, according to the following equation:—

$$2SeCl_4 = Se_2 + 4Cl_2.$$
4 vols. — 8 vols.

If the monochloride is stable, however, at such temperatures (which

we have great reason to doubt), the following reaction would take place:—

$$2SeCl_4 = Se_2Cl_2 + 3Cl.$$
$$4 \text{ vols.} \quad 2 \text{ vols.} \quad 6 \text{ vols.}$$

In either case the volume would be doubled. But when the vapour-density of the monochloride and of the tetrachloride was ascertained, there was no indication of a deposit of selenium in the bulb of the apparatus; we must therefore conclude that complete recombination ensued on cooling.

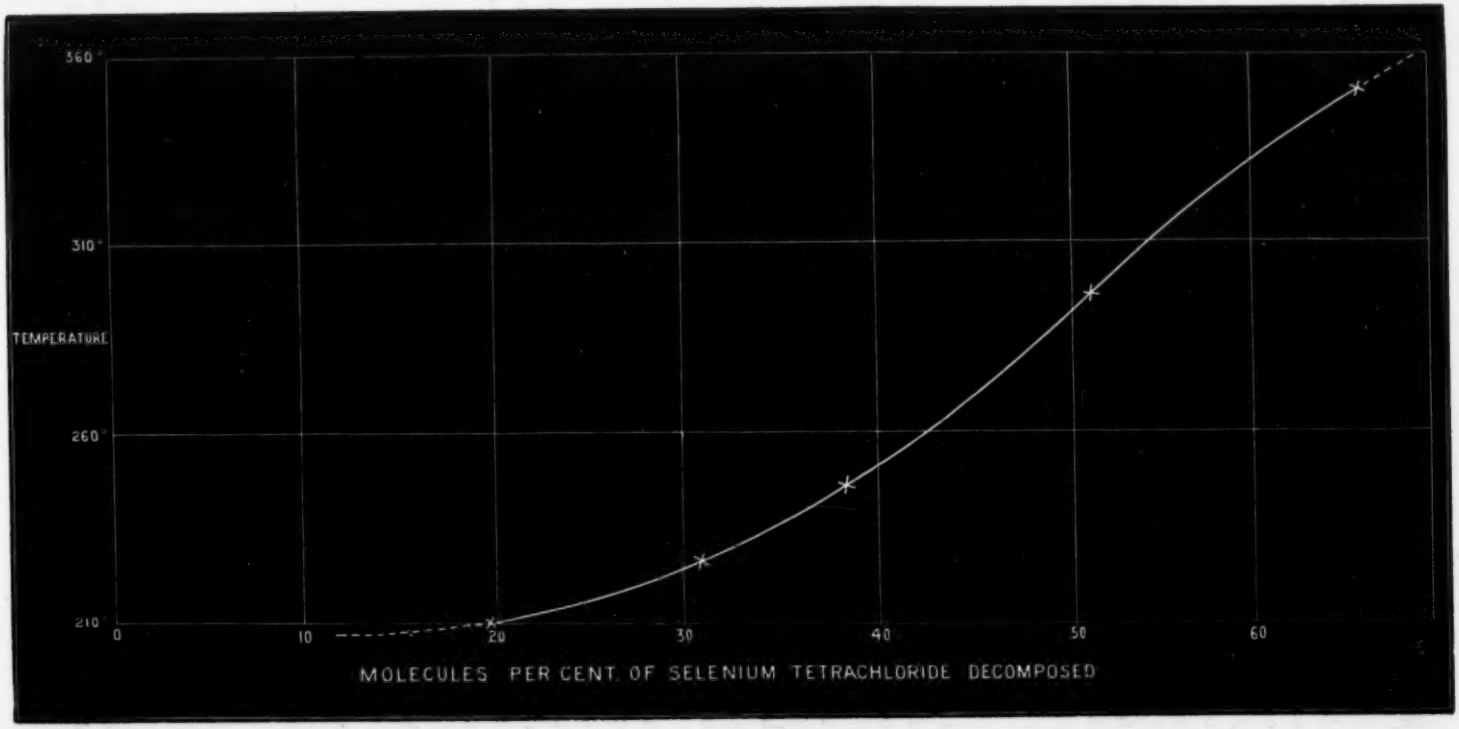
From the above numbers the percentage of molecules of tetrachloride decomposed was calculated by means of the formula—

$$p = \frac{100(D - d)}{d},$$

where p represents the percentage of molecules decomposed, D the theoretical vapour-density of selenium tetrachloride, and d the vapour-density determined by experiments of the undecomposed tetrachloride mixed with its products of decomposition. The results are seen in the following table:—

Temperature.	Percentage of molecules decomposed.
180°	0
200	0
210	19·48
225	30·88
245	38·23
295	51·53
350	65·74

These results are represented graphically in the accompanying figure.


360°
310°
260°
210°
TEMPERATURE
0
10
20
30
40
50
60
MOLECULES PER CENT. OF SELENIUM TETRACHLORIDE DECOMPOSED

It is to be observed that at a temperature approximating to 288°, 50 per cent. of the number of molecules of $SeCl_4$ originally present has been decomposed. This temperature is therefore the *absolute temperature of decomposition of selenium tetrachloride*. Dissociation is *nil* at 200°, and is found to amount to 19·48 per cent. at 210°. It appears to begin at about 205°. If the number of degrees between the temperature at which dissociation begins and the temperature at which 50 per cent. has dissociated be equal to the number of degrees between the latter and the temperature at which dissociation is complete, then at 371° selenium tetrachloride must have completely dissociated; for $288-205° = 83°$, and $288° + 83° = 371°$. That portion of the curve which has been investigated appears to point to such a temperature.

It is well known that when sulphur and bromine are mixed, a slight rise of temperature is noticed, which would imply the formation of a compound. But the temperature at which this compound dissociates must be a low one; for on distilling, the first portions of the distillate consist of almost pure bromine (Hannay, this Journal, **26**, 823; **33**, 284; Muir, *ibid.*, **28**, 145). We have found that bromine may be mixed with sulphur monochloride, S_2Cl_2, without any sign that a compound is formed; and it is extremely improbable that the bodies should combine, for even with chlorine, the tetrachloride of sulphur formed is stable only at very low temperatures.

On the other hand, if selenium monochloride is mixed with bromine in the proportion required by the equation $Se_2Cl_2 + 3Br_2 = 2SeClBr_3$, combination takes place at once, a solid crystalline substance of a yellow colour being formed. It is advisable to use a mixture of bromine and carbon disulphide in the preparation of selenium chlorotribromide, to moderate the otherwise violent action. The new compound is sparingly soluble in carbon disulphide, and it is freed from excess of bromine and monochloride of selenium by that solvent. It was freed from carbon disulphide by warming it and drawing a current of dry air over it.

On analysis, it gave the following numbers:—

1. Taken 0·2463 gram.

AgCl + AgBr	0·4780 = chlorine and bromine..	75·55	per cent.
Se	0·0550	23·34	„
Calculated for $SeClBr_3$,	chlorine and bromine..	77·60	„
„	„ selenide.....	23·39	„

2. Taken 0·3218. Se found 0·0720 = 22·37 per cent.

When first prepared this substance has a slight orange-yellow colour, but when kept for some time, it turns to a dark purple, probably owing to the action of light. It is deposited from its solution

in carbon disulphide in orange-coloured crystals; these crystals rapidly attract moisture from the air.

Its vapour-density was determined at 200° and at 260°.

	Temp.	Amount taken.	c.c. of air collected.	Temp. of air.	Pressure.	Vapour density.
I....	200°	0·0830	11·8	15·2	749·0 mm.	84·90
II....	260	0·0855	12·6	14·0	758·6 „	79·77

The theoretical vapour-density of $SeClBr_3$ is 177·38; dissociation is therefore complete at 200°, probably in accordance with the equation—

$$2SeClBr_3 = Se_2 + Cl_2 + 3Br_2.$$
$$4 \text{ vols.} \quad — \quad 2 \text{ vols.} \quad 6 \text{ vols.}$$

When the compound is warmed, bromine is evolved, and probably the monochloride is left; if the bromine is not allowed to escape, crystals of the chlorobromide are reproduced on cooling.

Another body, of the formula $SeBrCl_3$, was prepared by acting on selenium monobromide, Se_2Br_2, with chlorine. The monobromide was mixed with carbon disulphide, and a stream of chlorine gas passed through the mixture. A yellow-brown crystalline precipitate fell, which was dried in a current of warm air, after being washed with disulphide to remove excess of monobromide. It yielded the following numbers on analysis:—

1. Taken 0·4124 gram.

Selenium obtained 0·1245 gram = 30·18 per cent.

2. Taken 0·3050 gram.

AgCl + AgBr weighed	0·7110 = 0·2144 Cl_3 + Br..	70·29 p.c.
Se obtained	„ 0·0890	29·18 „
Calculated for $SeBrCl_3$,	chlorine and bromine	70·25 „
„ „	selenium	29·75 „

When heated, the substance evolves bromine, and yields a sublmiate of the tetrachloride. It does not melt at the ordinary pressure. It was hoped that interesting results would be obtained by taking its vapour-density at different temperatures, similarly to those given by the tetrachloride. The determinations made are shown in the following table:—

	Temp.	Amount taken.	c.c. of air collected.	Temp. of air.	Pressure.	Vapour density.
I..	179°	0·0777	7·95	22°	754·1	131·47
II..	205	0·0880	10·60	22	754·1	111·68
III..	208	0·0950	12·80	22	754·1	94·66
IV..	280	0·0800	16·82	22	754·1	63·98

At the temperature 179°, it would appear that the substance is un-

decomposed, for the theoretical vapour-density is 132·4; and at the temperature 280°, it appears to be completely resolved into its elements. The vapour-density 111·68 would correspond with 18·55 per cent. of the molecules having dissociated; and 94·66 with 39·87 per cent. But we are disposed to lay little weight on these numbers: for the dissociation is slow—much slower than that of the tetrachloride—and in every case but the first, bromine-vapour was distinctly seen in the vertical tube of the vapour-density apparatus, and a few minute drops of a red liquid condensed in the tube. It was impossible to hasten the operation so as to avoid diffusion. We do not therefore believe that the numbers in II and III given above represent the true vapour-densities, but we are sure that they are too high. It is evident, however, that this substance is stable at a higher temperature than the chlorotribromide, for at 200° the vapour-density of the latter points to complete dissociation.

There appears also to be a dichlorodibromide of selenium producible by acting with chlorine on a mixture of tetrabromide and dibromide of selenium in the proportion $SeBrSe_2Br_2$, or on a similar mixture of the chlorides with bromine. It is a brown-yellow crystalline powder. As it promised no results of theoretical interest, it was not investigated.

An attempt was made to produce a chloriodide of similar formula to the chlorotribromide, by dissolving iodine in calculated proportion in carbon disulphide and adding the solution to that of the monochloride. We failed, however, to isolate any definite substance. On evaporation of the disulphide, iodine invariably crystallised out, and the mother-liquor on evaporation deposited fresh crops of iodine crystals, and contained selenium monochloride. A chloriodide of the formula $SeClI_3$ is thus apparently unstable at ordinary temperatures.

The halogen compounds of selenium and sulphur may be thus compared :—

	Temp. of decomposition.
Sulphur tetrachloride, SCl_4	−17°
Sulphur dichloride, SCl_2.....	86
Sulphur monochloride, S_2Cl_2	?
Selenium monochloride, Se_2Cl_2	130—150 ?
Selenium dichloride, unknown.	
Selenium tetrachloride.....	288
Selenium chlorotribromide .....much below	200
Selenium bromotrichloride .....somewhat above	208

The numbers for the chlorides of sulphur are taken from results of Michaelis and Schifferdecker (*Ber.*, 1873, 993). It would thus appear

that the compound of sulphur with chlorine which contains the smallest amount of chlorine is the most stable, while that compound of selenium possesses greatest stability which contains the greatest proportion of chlorine. Both selenium and sulphur agree in the small stability of their bromides, although the stability of the bromides of selenium is greater than that of the bromides of sulphur.

X.—*Experimental Investigations on the Value of Iron Sulphate as a Manure for Certain Crops.*

By A. B. Griffiths, Ph.D., F.C.S. (London and Paris), Medallist in Chemistry and Botany, &c.

I have already published some researches* on the growth of *single* plants by the aid of iron sulphate, and having been engaged lately in certain investigations to ascertain, if possible, to what extent this mineral compound is useful as a manure when applied to field crops, I have now the honour of laying before the Chemical Society the results of my investigations on this important subject. Two plots of well-drained land in the neighbourhood of Bromsgrove, Worcestershire, were chosen. The analysis of the soil (which was collected by the Lawes and Gilbert method) gave the following results:—

	I.	II.
Silica and insoluble matter	80·75	80·74
Organic matter	4·92	4·90
Ferric oxide (Fe_2O_3).....	3·93	3·96
Alumina (Al_2O_3).....	2·92	2·89
Magnesia (MgO).....	0·50	0·49
Lime carbonate ($CaCO_3$).....	3·25	3·28
Lime sulphate ($CaSO_4$)	0·26	0·27
Potash (K_2O) and soda (Na_2O)	0·36	0·35
Phosphoric oxide (P_2O_5)	0·38	0·42
Moisture	2·73	2·70
	100·00	100·00

One plot of land was treated with the crystallised ferrous sulphate of commerce (the quantity applied being half a hundredweight to the

* "Researches on the Growth of Plants under Special Conditions" (*Chem. News*, **47**, 27, and *Chem. Soc. J.*, Abstracts, 1883, 496). "Chemico-Microscopical Researches on the Cell-Contents of Certain Plants" (*Chem. Soc. J.*, Trans., 1883, 195; and *The Journal of the Royal Microscopical Society*, August 1883, 536.

acre), and the other was left in its normal condition. Both plots of land are exposed to the same amount of sunshine and rainfall. On each plot of land I planted on the same day a certain number of bean seeds. These were allowed to grow until ready for gathering, when they were gathered and weighed, then allowed to dry and weighed again, with the following results:—

	Plot of land (manured with $FeSO_4$).		Plot of land (normal).	
	(1.) Weight when gathered.	(2.) Weight when dry.	(1.) Weight when gathered.	(2.) Weight when dry.
Total weight of crop (grain + straw).....	6783 lbs.	5882 lbs.	5210 lbs.	4487 lbs.

The plants grown by the aid of the iron manure yielded 56 bushels of grain, while the plants grown without this mineral manure yielded only 35 bushels of grain; so there is a marked difference in the weights of the produce of the two pieces of land. In fact, the iron manure has been of great benefit in aiding the growth of this plant.

A certain number of the plants grown on each plot of land were separately reduced with the greatest possible care to ashes. The plants were burnt (as described in my former paper) on a platinum sheet made in the shape of a muffle, and heated at a low temperature in a gas furnace. The ashes yielded on analysis the following results:—

(A.) *Analysis of Ash of Entire Plant.*

	Plants grown *with* iron manure.		Plants grown *without* iron manure.	
	I.	II.	I.	II.
Iron oxide (Fe_2O_3).....	4·221	4·230	1·063	1·052
Potash (K_2O).....	18·400	18·395	20·791	20·710
Soda (Na_2O).....	16·013	16·211	17·512	17·509
Lime (CaO).....	6·654	6·599	7·204	7·220
Magnesia (MgO).....	7·981	7·899	8·795	8·760
Silica (SiO_2).....	1·946	1·953	2·773	2·721
Phosphoric oxide (P_2O_5).....	41·902	41·899	37·941	37·920
Sulphuric oxide (SO_3).....	1·001	1·022	1·400	1·462
Sodium chloride.....	1·781	1·792	2·510	2·490
	99·959	100·000	99·989	99·844

(B.) The next table gives the analysis of the ashes of the *pods* minus the seeds :—

	Grown *with* iron manure.	Grown *without* iron manure.
Iron oxide (Fe_2O_3)	2·021	0·911
Potash (K_2O)	41·369	42·506
Soda (Na_2O)	2·900	3·604
Lime (CaO)	6·909	6·022
Magnesia (MgO)	7·103	7·400
Silica (SiO_2)	0·542	0·504
Phosphoric oxide (P_2O_5)	36·061	34·240
Sulphuric oxide (SO_3)	2·652	3·615
Chlorine	0·433	1·191
	99·990	99·993

(C.) In this table I give the analyses of the ashes of the *seeds* from plants grown with and without the aid of the iron manure :—

	With iron manure.	Without iron manure.
Iron oxide (Fe_2O_3)	0·572	0·576
Potash (K_2O)	42·491	42·489
Soda (Na_2O)	1·361	1·370
Lime (CaO)	4·700	4·702
Magnesia (MgO)	7·101	7·099
Silica (SiO_2)	0·840	0·837
Phosphoric oxide (P_2O_5)	38·810	38·820
Sulphuric oxide (SO_3)	2·512	2·520
Chlorine	1·613	1·586
	100·000	99·999

From these analyses (which were conducted with the greatest possible care) it will be seen—

1st. That by manuring the land with half a hundredweight of ferrous sulphate to the acre, the harvest was increased. The land which was manured yielded an increase of 1573 lbs. in the total weight of the crop when gathered; 1395 lbs. when dry (straw); and an increase of 21 bushels of grain over the crops grown without the iron manure.

2nd. When the ashes of the entire bean plants are submitted to analysis, it is found that the plants grown with an iron manure contain a much larger percentage of ferric oxide in their ash than the plants grown without an iron manure; and looking at Tables A and B, it is seen that the phosphoric oxide in the ashes increases as

the ferric oxide increases. Thus it will be seen that the composition of the ash of the bean plant is greatly influenced by the manure applied to the soil; but in Table C, which is the result of analyses of the seeds produced by plants grown with an iron manure, and seeds produced by plants grown in a soil without any added iron manure, the feature to be noticed is that the percentage numbers agree most closely in each case; thus giving additional support to the general law that the composition of the ash of the seed or embryo is very constant. From these experimental researches, I think I am safe in saying that for *certain* plants an iron manure in the form of a soluble sulphate is beneficial to their growth.

There is a precaution in the use of ferrous sulphate as a manure I may mention in passing. Last summer an entire crop of young cabbage-plants was almost killed by having the land manured with farmyard manure along with ferrous sulphate. I investigated the matter with the following results: that the carbonaceous matters of the farmyard manure reduced the sulphate to sulphide of iron; and acids acted upon this sulphide liberating sulphuretted hydrogen, which was the cause of the mischief to the little crop.

Appendix.

Observations on the Influence of Certain Rays of the Spectrum on the Growth of Plants growing in an Iron Manure.

In seven small flower-pots, each filled with the same kind of soil, treated with a known weight of iron sulphate, I sowed some mustard seeds. When the little plants had made their appearance above the soil, I exposed them for some hours each day to the coloured lights of the spectrum. No. 1 was exposed to the red part of the spectrum, No. 2 to the orange, and so on; after so many hours' exposure, they were removed to a dark place. This operation was performed for several weeks, each pot being exposed to its own part of the spectrum daily, until the plants had grown to a considerable size. The plants in each pot were then reduced to ashes and submitted to analysis, the following percentage of ferric oxide being found:—

						Per cent. Fe_2O_3 in ash.
Pot No.	1	exposed to	red	part of spectrum	gave	0·92
"	2	"	orange	" "	....	1·43
"	3	"	yellow	" "	....	2·51
"	4	"	green	" "	....	1·90
"	5	"	blue	" "	....	0·71
"	6	"	indigo	" "	....	0·20
"	7	"	violet	" "	....	0·15

The same number of seeds were placed in each flower-pot, and the plants, as they grew, were watered from time to time with a weak solution of ferrous sulphate (always of the same strength).

These experiments therefore show that the most active rays for absorption coincide with those of assimilation, and at the same time prove that the iron acts to a certain extent as a food for the chlorophyll granules, these being the active agents for the process of assimilation; and from the researches of Drs. Draper and Pfeffer and those of Cloez and Gratiolet, it is evident that the most favourable rays of white light are those lying between the yellow and green; for in their experiments the greatest amount of oxygen was evolved in this part; and therefore the largest amount of carbon is retained by this process of assimilation when the plants are exposed to this part of the spectrum. I think my researches as above described confirm their conclusions in another way; for I get the largest amount of Fe_2O_3 in the ashes of the plants exposed to the yellow or yellow-green part of the spectrum, or between Fraunhofer's lines D and E. From the above it will be seen that the rays near the least refrangible part of the spectrum are the most active in aiding the growth of plants; that there is a connection between chlorophyll and iron; and that if the iron be given within certain limits to a plant, it acts as a food of great value, most probably nourishing the chlorophyll granule; for I have found monoclinic crystals (as shown in my paper read before the Chemical Society on March 1st last) of ferrous sulphate near to the chlorophyll granules.

University of Illinois

XI.—*On the Decomposition of Silver Fulminate by Hydrochloric Acid.*

By Edward Divers, M.D., and Michitada Kawakita, M.E.

The behaviour of silver fulminate with hydrochloric acid is sufficiently different from that of mercury fulminate to make us desire to publish the fact without delaying to complete an investigation of the change.

Formic acid and hydroxyammonium chloride are produced as in the case of the mercury salt, but we can only as yet find *two-thirds* of the calculated quantity of each of these bodies. We get besides ammonia and a trace of hydrogen cyanide. Gay-Lussac and Liebig observed the production of ammonia from the silver salt. Mercury fulminate yields ammonia only when treated with the reducing acid, hydriodic acid (Carstanjen and Ehrenburg). We have as yet failed

to find what becomes of the rest of the carbon and some of the nitrogen: for the nitrogen in both hydroxyammonium and ammonium chlorides does not equal that of the fulminate. In decomposing mercury fulminate with hydrochloric acid, Carstanjen and Ehrenburg, somewhat strange to say, got only two-thirds of the nitrogen as hydroxyammonium chloride, while Steiner and we ourselves get the whole of it in this form.

A first product of the action of hydrochloric acid upon the silver salt is an acid striking a deep red with ferric chloride, even in presence of strong hydrochloric acid. This acid has been partly described by Gay-Lussac and Liebig. It is unstable. They state that it contains much chlorine and also nitrogen. The formation of this acid does not help us in any way to account for the proportions of carbon and nitrogen which we have failed to find. We may add that our silver fulminate gave us 71·79 per cent. silver, theory requiring 72 per cent.

XII.—*Supplementary Note on Liebig's Production of Fulminating Silver without the Use of Nitric Acid.*

By Edward Divers, M.D., and Michitada Kawakita, M.E.

In a recent communication to the Society on the subject of this note, we stated our inability to confirm Liebig's statement that nitrogen trioxide passed into an alcoholic solution of silver nitrate gives silver fulminate. We have since succeeded in getting a very small quantity of fulminate in this way, but under conditions which deprive its production of all significance or peculiarity. We proceeded in the following manner.

Silver nitrate was dissolved, but not to saturation, in somewhat more than 100 c.c. of cold alcohol of specific gravity 0·825, and into the solution nitrogen trioxide was passed continuously for a very long time—about three hours. For nearly two hours the gas was almost wholly absorbed, but for the last hour very much of it escaped. During the period of absorption nitrous ether escaped continuously, and in consequence probably the liquid did not rise very much in temperature. But during the last hour it grew comparatively hot, sometimes as high as 60—65°. The next morning a very small quantity of fulminate was found to have crystallised out. In amount

it could not have been so much as even half a centigram, while there was present in the solution more than a gram of silver.

On examining the mother-liquor of this small quantity of fulminate, it was found to measure much less than the original solution, and to be intensely acid. Some aldehyde was present, but it consisted principally of alcohol, water, and nitric acid, besides silver nitrate. The nitric acid was present in the proportion of 2 grams (hydrogen nitrate) in 10 c.c. of the mixture, and the alcohol and water were in the proportions forming "proof" spirit. We saw at once that we had almost certainly only a case of the ordinary formation of silver fulminate from a heated mixture of nitric acid and alcohol.

We verified this view of the matter by making a mixture of nitric acid, alcohol and water in the above proportions, dissolving silver nitrate in it, and then heating it on the water-bath. After it had been kept at 65° for nearly ten minutes, a very little fulminate formed, just as in the nitrous acid experiment. On continuing to keep it at this temperature for about twenty minutes more, the mixture became so active as to grow hotter of itself, and then to deposit an abundance of silver fulminate.

The next experiment—or rather set of experiments, for each kind was repeated—was to take the same mixture and, keeping it cold, to pass nitrogen trioxide into it in extreme excess. Proof spirit, unlike spirit of greater strength, only imperfectly absorbs the gas, but this was passed until the liquid became blue, and even green, by its dissolution. At length a small deposit actually occurred, but of a substance not yet identified by us, and which was certainly not fulminate (or oxalate). We hope at a future time to examine this substance. Fulminate is therefore not formed so long as the mixture remains cold.

It is thus made evident that in getting a trace of fulminate by the use of nitrogen trioxide, we have still not succeeded in getting any from alcohol, nitrogen trioxide, and silver nitrate, without both the presence of nitric acid and the operation of heat. Whether Liebig allowed his solution to grow hot and very acid we cannot tell, not having been able to refer to his paper.

XIII.—*On Hyponitrites.*

By Edward Divers, M.D., Principal, and Tamemasa Haga, Instructor in Chemistry, Imperial Japanese College of Engineering, Tokio.

The hyponitrites were discovered by one of us in 1871, and briefly described by him in a paper which appeared in the *Proceedings of the Royal Society* of that year.* In 1877, Zorn issued the first of a series of communications on the same subject which has been continued by him nearly up to the present time (*Ber.*, **10**, 1306; **11**, 1630 and 2217; **12**, 1509; **15**, 1007 and 1258). Closely following Zorn's first paper, came one from van-der-Plaats (*Ber.*, **10**, 1507), and in the next year another by Menke (*Chem. Soc. J.*, Trans., **33**, 401). Lastly, Berthelot and Ogier (*Compt. rend.*, **96**, 30 and 84; *Chem. Soc. J.*, 1883, Abstr., 422) have recently published, in two parts, a paper on the silver salt.

The authors of the present note have been together engaged for some time, in spare moments, on the investigation of hyponitrites, and although they have, as yet, but little actually new to make known, they are led to publish without further delay part of what they have done, by the statements occurring in the papers of other workers on the subject, and more especially by the important ones made by Berthelot and Ogier. These papers, besides containing additions to the knowledge of hyponitrites, go over most of the work already done by one of us, and give results which sometimes confirm, but sometimes conflict with, his statements.

Composition of Silver Hyponitrite.

One of us has given the composition of the silver salt as being silver, nitrogen, and oxygen in the proportions of 1 atom of each. When he published this statement, the evidence in support of it was such as to leave no doubt in his mind as to its accuracy, although he had then only made determinations of the silver, and obtained quantities

* *Note by Edward Divers.*—It may have been supposed, from my silence upon the subject of the hyponitrites for a number of years, that I had ceased to be much interested in them, or to recognise the obligation that I was under to proceed with their investigation. Such, however, has not really been the case, and only unavoidable circumstances—more especially other active occupations—have prevented me from bringing any part of the investigation to a state fit for publication. I have now the benefit of the co-operation of my former pupil, Mr. Haga, and if I can retain this, I hope that some progress will from this time be made in the investigation, although it may still not be very rapid.

which were not closely concordant, and moreover about 1 per cent. too low. He stated that the salt slightly decomposed when it was heated to expel traces of moisture, and contained in consequence, sometimes when prepared for analysis, traces of brown or black matter, and he suggested that the silver was too low through the presence of moisture and other impurities. This explanation of the deficiency of the silver was not indeed very satisfactory, but his assertion that there could be no doubt as to the composition of the salt was justified, we think, by considerations such as the following, even at that time when other facts were wanting in support of it.

No other element had been found in it, but a minute trace of hydrogen sufficient to form water with only a very small fraction of the oxygen. It appeared to be a well-defined substance which could be repeatedly redissolved and reprecipitated without changing its properties. The amounts of silver found approached the calculated quantity closely, and yet varied among themselves so as to suggest the presence of impurity in the several portions analysed, probably in the form of products of decomposition. Evidence that such impurities were present was not wanting. The salt could not be represented as mixture of two substances of simple composition without assuming one to be present in small quantity only. Another formula could not be taken for it that would not be at least as complex and improbable as the one recently adopted by Berthelot and Ogier of $Ag_4N_4O_4$. Its mode of formation and the main facts of its decomposition pointed to the composition given to it. Lastly, its constitution as hyponitrite was the one in accordance with the simple constitution of other oxy-nitrogen salts.

These considerations, which still hold good, and which we offer in justification of the inference then made, it might be deemed unnecessary here to detail, because the correctness of this inference has been fully affirmed by Zorn, by van-der-Plaats, and by Menke, who have all published their success in preparing the salt pure for analysis, apparently without difficulty and without taking special precautions—this success leaving no longer any need for the inference. But it can hardly be looked upon as unnecessary, now that Berthelot and Ogier have asserted that the amount of silver in the hyponitrite is not quite the lowest even which one of us had found it to be, and less therefore than that required by the formula AgNO, and that Zorn, Van-der-Plaats, and Menke could not have got a salt answering in composition to this formula, and only through its decomposition by the heat they all employed could they have got the required percentage of silver.

Very many careful experiments of our own confirm the accuracy of this statement of Berthelot and Ogier. Before, indeed, their paper

was published, we had learned that without decomposition it seemed to be impossible to obtain, by the method of preparation employed by all of us in common, higher numbers for the silver than the lowest published by one of us.

This circumstance did not, however, lead us to doubt for a moment that the hyponitrite had the simple composition attributed to it, and it was to us a matter of astonishment to see Berthelot and Ogier giving a new formula based upon only the evidence they adduced. They indeed admit hesitation in proposing their new formula, but find reason for so doing in the results of their investigation of the quantitative reactions of the salt. We proceed to summarise their paper so far as is necessary.

They prepared the salt and purified it by dissolution in nitric acid and reprecipitation with ammonia, as one of us directs, and dried the washed salt *in vacuo* at ordinary temperatures in the dark. Thus they obtained a preparation free from any reduced silver, but containing some water. We frame the subjoined table of their results and calculations:—

	Found.			Omitting water.		Calculated.	
	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	$Ag_4N_4O_5$.	AgNO.
Silver	75·3	75·0	75·3	76·2	76·1	76·1	78·3
Nitrogen.....	9·6	9·6	—	9·7	9·8	9·9	10·1
Water.....	1·1	1·5	—	—	—	—	—
Oxygen by diff.	14·0	13·9	—	14·1	14·1	14·0	11·6

They mention also a percentage of 75·5 silver. They regard the water as non-essential, and give the salt the formula $Ag_4N_4O_5$, which, as will be seen, agrees most closely with their analyses. Not contenting themselves with these, they took the pains to verify the correctness of the above ratios of the elements by quantitative estimations of the products of the decomposition of the salt by heat, by dilute sulphuric acid, and by bromine. Some of the results they thus gained we expect to discuss in a future communication.

The remarkable thing to us about their investigation is that they should not have been induced by some consideration of the strange constitution such an acid as $H_4N_4O_5$ must have, and of the probability that they might be dealing with a mixture of hyponitrite with nitrite or nitrate, to test the effect upon their preparations of some variation in the method of purification. For there is nothing to be found in the results of their extended examination of the reactions of the substance in their hands, that is not quite consistent with the assumption of its having been a mixture of hyponitrite with nitrite or

nitrate, excepting perhaps the insolubility, apparent or real, of such a salt if present. However, they seem to have felt no need for such testing, and from their paper it stands uncertain whether they even worked with more than one preparation in their three direct analyses.

For ourselves, with the facts before us that the hyponitrites would, as products of the action of sodium, not improbably be readily oxidisable; that nitrites, including silver nitrite (Divers), undergo atmospheric oxidation; and that our preparations varied in composition, we felt that our task should be to endeavour to purify the hyponitrite from firmly adhering nitrite or nitrate, or to protect the salt from oxidation during drying, or to do both these things, and in all cases to be specially on our guard against any decomposition by heat.

The results we have obtained in this work deprive Berthelot and Ogier's formula of all claim to be accepted before any other that might be devised to express the composition of some mixture of hyponitrite with nitrite or nitrate, obtainable with tolerable uniformity by some special routine in preparing it. They also show that hyponitrite very nearly if not quite pure, can be prepared. We now give an account of some of our experiments.

The silver hyponitrite we analysed was prepared in comparatively small quantities at a time, and was preserved under water in the dark, after undergoing a first purification by one or more repetitions of dissolution in nitric acid, and reprecipitation by ammonia or sodium carbonate. For each analysis a portion was submitted to a separate and further treatment with nitric acid and sodium carbonate.* Except where mentioned, the hyponitrite was washed with acetic acid to remove any silver carbonate that might be present. A valuable property of sodium carbonate for our purpose was that of decomposing silver nitrate and nitrite without having any action upon hyponitrites.

I. Washed on a filter and dried on it, in the dark, over sulphuric acid in a vacuum, without heat, 0·4734 gram of hyponitrite, dissolved in nitric acid and decomposed by hydrochloric acid, gave 76·58 per cent. silver.

II. Treated in the same way, 0·5483 gram gave 76·73 per cent. silver.

* We replaced the use of ammonia for reprecipitating from nitric acid, originally employed by one of us and afterwards by others, by that of sodium carbonate, for one reason because we noticed a paleness in colour of some of our precipitates, which appeared to be due to the ammonia combining to some extent with the hyponitrite, but we are by no means certain that this precaution—any more than some others, such as the screening from light—was really needed.

III. Not liking the paper-filter because it blackened a little, and necessitated the selection of yellow salt from discoloured portions, and further drying in a watch-glass, we no longer used it, but this time tried an asbestos filter. We also dried the salt in this case, and all others after it, in a tube connected with a Sprengel pump, and holding much sulphuric acid, which we will presently describe more fully. In this analysis 0·3369 gram hyponitrite gave 76·54 per cent. silver.

IV. The drying was effected this time in a capsule placed in a desiccator, and then in a tube connected with the Sprengel pump. Hyponitrite, 0·2760 gram, gave 76·19 per cent. silver. In these four determinations of silver, as well as in all those which follow, the salt dissolved after drying, in both nitric acid and ammonia, without leaving a trace of insoluble matter.

We had thus in the above-described experiments obtained more than 1 per cent. silver higher than Berthelot and Ogier had got, by a proceeding almost identical with that followed by them, and no more open to objection than theirs.

Berthelot and Ogier ..	75·3	75·0	75·3	75·5
Divers and Haga	76·58	76·73	76·54	76·19

Their preparations, however, contained more than 1 per cent. of water, whereas ours, we believe, were nearly, if not quite free from water. By allowing for this water they calculated their silver to be (see table already given) 76·2 and 76·1 per cent.; about half a per cent., that is, less than ours. Any way regarded, here is an excess of silver found by us that is inconsistent with the formula $Ag_4N_4O_5$, requiring as this does 76·1 per cent.

The difference between their results and ours being readily explicable on the supposition that our preparations contained less nitrite or nitrate than theirs, we tried to get other percentages of silver by variations in preparing the salt for analysis. We had observed that silver hyponitrite did not always possess even the slight solubility in water sufficient to cause an opalescence with hydrochloric acid on standing, which one of us had described it to have, it being sometimes in fact practically insoluble in water. We were thus led to suppose that its apparent slight solubility at other times might be due to oxidation. Indications of the presence of nitrite and nitrate were to be found in the wash-water, even after protracted washing, but then this might be only some obstinately adhering and slowly washing out. Water deprived of air by boiling showed, however, a distinctly less solvent power than other water, and it therefore became tolerably certain that atmospheric oxidation of the hyponitrite did occur. The

next two experiments were consequently instituted to settle the point.

In two experiments purified hyponitrite was left for about fifteen days or so with water in a covered basin in the dark, or until the water had almost dried up. The drying was then finished in the Sprengel vacuum for two days by the side of sulphuric acid.

V. 0·1188 gram gave 75·63 per cent. silver.

VI. 0·2305 gram gave 75·82 per cent. silver.

The hyponitrite had thus in these cases, as expected, suffered some oxidation, and had given us products nearly as low in silver as those analysed by Berthelot and Ogier—or, regarding as we do our preparations as having been dry, or nearly so, a still lower percentage than theirs.

It seemed to us most remarkable that a silver salt should contain 1·1—1·5 per cent. of water, as Berthelot and Ogier had found the hyponitrite to do, after drying *in vacuo* over sulphuric acid, and in order to determine to what extent water might be present in our own preparations, we tested two of them. No precautions against slight atmospheric oxidation were taken in preparing them. They were dried at the ordinary temperature in the Sprengel vacuum with sulphuric acid for about two days. The tube containing the dried salt having been sealed off from the sulphuric acid holder, was connected on one side with drying tubes through which carbon dioxide was passing, and the sealed point broken off. The other point having also been broken, the tube was on that side connected with a tube of heated copper turnings and a weighed calcium-chloride tube. The tube was then heated so as to decompose the hyponitrite, and the current of carbon dioxide continued for some time. An increase in weight in the calcium-chloride tube was found to have occurred.

VII. Hyponitrite yielding 0·0006 gram water was found to have contained 0·3041 gram silver. Assuming that the salt contained 76·5 per cent.—and a small error in this assumption is of no moment—we find a percentage of water amounting to 0·15.

VIII. With 0·6258 gram silver was found 0·0017 gram water, equal to 0·21 per cent.

These quantities of water are only the seventh of what Berthelot and Ogier got, but even so, their presence is abnormal. Blank experiments have made us certain of our results, but we believe this water may have come from some organic impurity, and not have been mere moisture. This is a matter we have yet to investigate. We have assumed that our other preparations contained only such small quantities as here found.

To avoid oxidation during washing, we now used subsidence and decantation instead of filtration, and transferred the salt suspended in

water to a drying tube to be connected with the Sprengel pump as in other experiments. It is necessary briefly to describe this tube. Tubing of about 2 cm. diameter was drawn out at the ends, and at an intermediate point much nearer one end than the other. In this way the tube formed two receptacles, one for the hyponitrite, and one, about 3 decim. long, for the sulphuric acid. The contracted part of the tube which separated them was bent into a rising curve, and the drawn-out ends of the tube were also bent into convenient form. The hyponitrite was introduced into the smaller receptacle by means of a slender funnel in this case, but in some other cases by means of a slender siphon. This end of the tube was next sealed off and sulphuric acid run into the other receptacle, which was then put in connection with the Sprengel pump. When the evaporation of the water—dry ice that is—was finished, the tube was sealed off from the pump, and after standing for the desired time, the two receptacles were separated also by sealing. Just before weighing the tube of hyponitrite, one end was broken off to admit air.

IX. Silver hyponitrite, 0·1302 gram, thus prepared, gave 76·59 per cent. of silver, and therefore no improvement in return for our precautions.

X. This experiment was like the last, but with the difference that after drying in the vacuum at the ordinary temperature, the receptacle holding the hyponitrite was heated to 60° C. for two hours before sealing off from the pump. Not a trace of gas was liberated, and the salt remained unaltered in appearance, besides being completely soluble in ammonia and dilute nitric acid. The quantity of hyponitrite taken was 0·5247 gram, and the percentage of silver found 77·06, which was a marked improvement upon previously obtained results.

Carbon dioxide has no sensible decomposing action upon silver hyponitrite, but, when in solution, dissolves it slightly, like acetic acid. In order therefore to exclude air during the purification of the hyponitrite, its dissolution in nitric acid, reprecipitation with sodium carbonate, and washing with de-aërated water, with dilute acetic acid, and again with water, were all carried on in a closed bottle fitted with tapped funnel, carbon-dioxide supply tube, and exit siphon-tube. When raised, the siphon-tube led off gas, and, when pushed down, either washings or hyponitrite suspended in water at pleasure. This tube was so narrow that the silver hyponitrite could be easily pressed up it with the water by the carbon-dioxide gas, in spite of its tendency to subside. By means of this siphon the salt, when ready, was transferred to the drying tube previously filled with carbon dioxide, and charged with sulphuric acid. The drying tube was then connected with the Sprengel pump.

XI. Hyponitrite, 0·2737 gram, gave 77·13 per cent. of silver.

XII. In an experiment the same as the last, but in which the effect of a final heating to 60° C. for nearly two hours was tried, hyponitrite, 0·2703 gram, gave 77·09 per cent. of silver. We were therefore disappointed in the effects of heating, and did not again resort to its use.

The numbers, 77·06, 77·13, and 77·09, were still a little more than 1 per cent. below the percentage for the formula AgNO, but nevertheless were about 1 per cent. higher than that required by Berthelot and Ogier's formula, and 2 per cent. above their actual numbers. Considering now that we might perhaps succeed in removing obstinately adhering nitrite or nitrate by repeated dissolutions and reprecipitations in the absence of air, we made two experiments in accordance with this notion. In the bottle, arranged as already described for working in an atmosphere of carbon dioxide, three dissolutions and reprecipitations with intervening washings were made. The sodium carbonate used for precipitating must be of special service in decomposing any silver nitrite and nitrate. In the first experiment we used acetic acid after each precipitation in order to dissolve out any silver carbonate that might have been formed. In the other experiment we omitted the use of the acetic acid after the final precipitation. We have sufficient reason for believing that no silver carbonate remained with the hyponitrite in this case, but will point out that supposing a trace did remain, it would have no effect upon the percentage of silver, for carbonic acid and hyponitrous acid have the same combining weight.

XIII. Hyponitrite, 0·2452 gram, gave 77·69 per cent. of silver.

XIV. Hyponitrite, 0·2977 gram, gave 77·53 per cent. of silver.

These are the highest percentages we have as yet got—0·8 to 0·6 per cent. of silver too low for the formula AgNO, but we fully expect to improve upon them. On comparing the analyses we have recorded in this paper with those published in the first communication on the subject by one of us, it will be seen that there is very little difference between their results.

Our experiments are incomplete, but we believe them sufficient to show beyond reasonable doubt that silver hyponitrite prepared in the usual way, is a salt of the composition AgNO, although mixed with products of its oxidation.

On the Preparation of Alkali Hyponitrite Solution.

Three distinct ways of preparing alkali hyponitrites have been published. The first, by one of us, is the reduction of alkali nitrite in solution by sodium or potassium amalgam; the second, by Menke,

is the reduction of fused nitrite by iron; and the third, by Zorn, is the reduction of dissolved alkali nitrite by ferrous hydroxide. In all three cases nitrate may be used to begin with in place of nitrite.

First Method.—In a paper of which we have only been able to see abstracts, Zorn expresses a preference for the use of ready-prepared nitrite for reduction by sodium.* With regard to his preference we may point out that the advantage of starting with nitrite is not so certain as it may seem to be. There must be taken into consideration the comparative purity of easily obtained nitrate and the usually great impurity of commercial nitrite, causing waste of much silver hyponitrite in the process of purification. Preparation of the nitrite in one's own laboratory removes this disadvantage, it is true, but still leaves the trouble to be taken. It must be further remembered that nitrite thus prepared in the ordinary way contains still a considerable quantity of nitrate, so that the saving of sodium for deoxidising is less by far than half. Unless, too, the lead process be used, heating the nitrate in a cast-iron or even wrought-iron pot imparts phosphate to the salt, and we know of no very easy and satisfactory way of purifying silver hyponitrite from phosphate.

The preparation of hyponitrite by electrolysing a solution of alkali nitrite with mercury as the negative electrode, has also been described by Zorn. This is in reality a modification of the sodium-amalgam process. Its success is very interesting, for in the absence of mercury, as Thorpe has shown, the electrolysis of solution of sodium nitrite yields hydrogen and sodium hydroxide at the negative pole, and no hyponitrite anywhere. When mercury is used, some of the sodium formed is preserved in the mercury almost from the first, and soon becomes comparatively stable in it through the accumulation of sodium hydroxide in the solution. After a time, and before the completion of the reduction of the nitrite, the mercury, if not too abundant, grows pasty and even semi-solid from the presence of much sodium. It is evident that it is this sodium which converts the nitrite to hyponitrite and some hydroxylamine, just as much here as in the ordinary amalgam process. We have not seen Zorn's paper, and it may be that he has himself given this explanation. For the

* From the abstract in *Watts's Dictionary*, Third Suppl., the reduction of nitrite to hyponitrite by Zorn might appear to be something new, which is not the case. One of us, in the original paper, mentions, in describing the production of hyponitrite from sodium and nitrate, that the metal first converts the nitrate into nitrite which is then easily obtainable, and that the nitrite is next reduced to hyponitrite by more sodium. Even the use of nitrite to begin with was too obvious from the first to have escaped his attention, although no mention of its trial—or, indeed, of any unessential particulars of the preparation of hyponitrite—occurs in this paper. All hyponitrite is the result of the reduction of nitrite when the sodium process is used, and doubtless also in other processes.

same reason we do not know the details of his mode of proceeding. We ourselves kept the positive electrode apart from the nitrite solution by enclosing it in a porous cell, and in this we put potassium hydroxide solution. Otherwise the sodium is formed by the decomposition of some of the nitrite—a very serious matter, because two atoms of sodium are necessary to deoxidise one molecule of sodium nitrite. As with the ordinary amalgam process, the yield of hyponitrite is far below the calculated quantity. We have spent much time upon this process, with the result that, situated as we are, we much prefer sodium to the galvanic battery to work with in making hyponitrite.

It is worthy of note that Zorn here prefers to make his sodium amalgam at the moment (and at the cost of his nitrite ?) instead of previously preparing it, while in his first process he chooses to prepare his nitrite first, instead of making it at the moment and at the cost of his sodium.

Second Method.—Menke heats potassium or sodium nitrate with iron-filings, and with or without sodium carbonate, for an hour after deflagration has taken place, preferring a charcoal fire as the source of heat. We have followed his instructions—which, we suggest, might with advantage have been fuller—but we have hitherto failed to get any hyponitrite. Zorn, too, states that he has tried Menke's process many times and in many ways, and has always entirely failed. He considers that Menke has mistaken phosphate for hyponitrite of silver. But we find given the determination not only of the silver but of the nitrogen in the salt, and a description of the sodium salt in crystals. Menke, besides, seems not to have been off his guard against mistaking phosphate for hyponitrite, although he tells nothing of the method he adopted for distinguishing and separating the hyponitrite from the phosphate which, with cast iron especially, he must have had present in quantity.

Third Method.—Zorn has described in his last published paper a third method of making hyponitrite by using ferrous hydroxide as the reducing agent. We have repeatedly tried this method, but have hitherto been disappointed in getting any success with it. We have not yet, however, given that rigorous examination to the process which alone would lead us to say that the process will not eventually succeed in our hands. Reduction proceeds readily enough, but we have not found any hyponitrite among the products. We intend to make further experiments.

XIV.—*The Decomposition of Ammonia by Heat.*

By William Ramsay, Ph.D., and Sydney Young, D.Sc.

It has long been known that when ammonia gas is passed through a red-hot porcelain tube, or when it is exposed to the electric spark for some time, decomposition into nitrogen and hydrogen ensues. Attempts have also been made to bring about the combination of free nitrogen and hydrogen, but these have been attended with but slight success. Thus Deville noticed that when ammonia gas is exposed to the electric spark in a closed tube, there always remains a small quantity of the compound undecomposed, for by the introduction of a little hydrochloric acid gas a cloud is produced (*Annalen*, **135**, 104). He also found that the presence of hydrochloric acid hindered the decomposition of ammonia. An attempt to bring about the synthesis of ammonium chloride by the passage of hydrochloric acid gas, nitrogen, and hydrogen, through a tube heated to dull redness, led to no result, even when spongy platinum was placed in the tube (*Annalen*, **127**, 281). Deville, however, found that when the electric spark was passed through a mixture of nitrogen, hydrogen, and hydrochloric acid, a certain quantity of ammonium chloride was formed, and, in his ingenious apparatus designed to imitate the action of the spark, and consisting of a porcelain tube heated to redness, along the axis of which was placed a metal tube cooled by a stream of cold water, he succeeded in bringing about the same result. The quantity of sal-ammoniac formed was, however, very small (*Annalen*, **135**, 104).

Donkin, also, has recently shown that ammonia may be formed in small quantity by the passage of the silent discharge through a mixture of nitrogen and hydrogen (*Proc. Roy. Soc.*, **21**, 281). This has recently been confirmed by E. Johnstone (*Chem. News*, Dec., 1883). It is stated in *Watts's Dictionary*, vol. i, p. 183, that ammonia is decomposed by passage through a red-hot porcelain tube containing copper or iron wire, and to a less extent when gold, silver, or platinum wire is employed.

But little, however, is known as regards the temperature at which decomposition takes place, or as to the influence of the material of the vessel or tube containing the gas. It appeared interesting, therefore, to study these points more carefully than has yet been done.

The ammonia gas was generated by gently warming a concentrated aqueous solution of ammonia, and was dried by passing it through

three bottles containing quicklime, and then led through a tube heated by a Fletcher's furnace. The undecomposed ammonia was estimated by absorption in a known quantity of standard sulphuric acid and subsequent titration of the unsaturated acid, while the mixed nitrogen and hydrogen were collected in a suitable vessel and their volume measured. The temperature of the furnace was ascertained approximately by the fusion of salts placed on small pieces of platinum-foil lying on the surface of the tube. Thus, according to Carnelley, calcium chloride melts at 719°, and potassium chloride at 734°, and if the former salt liquefied, while the latter remained solid, the temperature was taken to be between 719° and 734°.

The percentage of ammonia decomposed was calculated as follows:—

v = volume of standard sulphuric acid taken.

v' = volume of standard soda solution required to neutralise the excess of acid.

1 c.c. of standard acid contains 0·0468 gram H_2SO_4, and therefore neutralises 0·0162 gram NH_3.

Therefore the amount of undecomposed ammonia = 0·0162 $(v - v') = x$.

The volume of the mixed gases at $t°$ and p mm. = V c.c.

The tension of aqueous vapour at $t° = \tau$.

Therefore the volume of mixed gases at 0° and 760 mm. = $\frac{V(p - \tau)}{(1 + 0{\cdot}003665t)760} = V'$.

1 c.c. of nitrogen at 0° and 760 mm. = 0·0012562 gram.

3 c.c. of hydrogen at 4° and 760 mm. = 0·0002668 gram.

Therefore 4 c.c. of the mixed gases weigh 0·0015250 gram, and 1 c.c. of the mixed gases weighs 0·00038125 gram.

Hence the weight of ammonia decomposed = 0·00038125 $V' = y$.

And the percentage of ammonia decomposed = $\frac{y \times 100}{y + x}$.

In the first series of experiments a porcelain tube filled with broken pieces of porcelain was employed with the following results:—

Temperature.	Weight of ammonia decomposed.	Weight of ammonia undecomposed.	Percentage of ammonia decomposed.	Mean.
500°	0·00678	0·43902	1·52	1·575
„	0·00907	0·54756	1·63	
520	0·00946	0·35316	2·61	2·53
„	0·00923	0·32902	2·73	
„	0·00703	0·28188	2·43	
„	0·00720	0·29970	2·35	

Temperature.	Weight of ammonia decomposed.	Weight of ammonia undecomposed.	Percentage of ammonia decomposed.	Mean.
600°	0·04493	0·19880	18·43	18·28
„	0·04486	0·20250	18·14	
620	0·04182	0·13446	23·72	25·58
„	0·04503	0·11502	28·79	
„	0·04560	0·14255	24·24	
680	0·04517	0·08586	34·47	35·01
„	0·04636	0·08910	34·22	
„	0·04629	0·08100	36·36	
690	0·04542	0·05832	43·78	47·71
„	0·04542	0·04212	51·88	
„	0·04542	0·05022	47·49	
810 to 830° ..	0·04431	0·02754	61·67	69·5
„ „ ..	0·04772	0·01620	74·66	
„ „ ..	0·04613	0·01134	80·27	
„ „ ..	0·34285	0·14256	70·63	
„ „ ..	0·34561	0·20412	62·87	
„ „ ..	0·36264	0·15390	67·04	

The want of uniformity in the results at the higher temperatures appears to be due to two causes—(1) the difficulty in keeping the temperature of the tube constant; thus in the last series the tube was at one time very nearly at 810°, and at another at about 830°; (2) The variable rapidity of the current of gas, which was found subsequently to exercise great influence on the amount of decomposition, and this might be anticipated, since there is practtially no recombination of nitrogen and hydrogen to form ammonia.

A second series of experiments was made with an iron tube filled with broken pieces of porcelain.

Temperature.	Weight of NH_3 decomposed.	Weight of NH_3 undecomposed.	Percentage of ammonia decomposed.	Mean.
507—527°	0·04432	1·01410	4·19	4·15
„	0·02303	0·53622	4·12	
600° (*a*).....	current very fast.			
„	0·04644	0·17658	20·82	21·36
„	0·04540	0·17344	20·76	
„	0·04527	0·15522	22·49	
„ (*b*).....	current much slower.			
„	0·04527	0·08586	34·44	34·44
628	0·04733	0·02268	67·61	65·43
„	0·04558	0·02592	63·75	
„	0·04558	0·02106	68·40	
„	0·34980	0·21465	61·97	

Temperature.	Weight of NH_3 decomposed.	Weight of NH_3 undecomposed.	Percentage of ammonia decomposed.	Mean.
676—695°	0·35407	0·16524	68·02	66·57
„	0·36473	0·19926	64·67	
„	0·35762	0·17334	67·35	
„	0·35941	0·18306	66·25	
730	0·34840	0·02268	93·89	93·38
„	0·35459	0·02106	94·39	
„	0·35034	0·02268	93·92	
„	0·35850	0·03402	91·33	
780	vol. = 1 litre	—	100	100
„	„	—	100	

It is to be remarked that in all these experiments with broken porcelain, the surface became blackened, owing, doubtless, to the reduction of the lead used in the enamelling. The surface was consequently blistered, and possibly to some extent porous.

The gas was then passed through a plain glass combustion tube lying in the iron tube, which was heated to 780°.

Weight of ammonia decomposed.	Weight of ammonia undecomposed.	Percentage of ammonia decomposed.
0·00571	2·4056	0·24

That the small quantity of gas collected was really a mixture of nitrogen and hydrogen was proved by its burning quietly with a colourless flame as usual.

The ammonia was then passed through a glass tube quite filled with fragments of broken combustion tubing to increase the surface. The temperature was again 780°, but rose slowly.

Weight of ammonia decomposed.	Weight of ammonia undecomposed.	Percentage of ammonia decomposed.	Mean.
0·01016	0·7776	1·29	1·72
0·01020	0·6042	1·66	
0·01040	0·5540	1·84	
0·01720	0·8019	2·10	

A glass tube was then filled with strips of ignited asbestos cardboard, which being porous should expose a large surface to the gas.

Temperature.	Weight of ammonia decomposed.	Weight of ammonia undecomposed.	Percentage of ammonia decomposed.	Mean.
520°	0·00788	0·2641	2·90	2·90
780	vol. = 1 litre	—	100	100
„	„	—	100	

On passing dry ammonia through a plain iron tube heated to 780° the whole of the ammonia was decomposed, as far as could be ascertained by volumetric analysis.

If, however, the tube was partially oxidised, water was formed, and only about 95 per cent. of the gas was decomposed.

The effect of metallic surfaces on the decomposition of ammonia was further studied by placing several lengths of iron and copper wire in a glass combustion-tube. With the iron wire at 760°, 76 and 74·3 per cent. of ammonia was decomposed, while with the copper wire, under similar conditions and at the same temperature, only 2·0 per cent. was decomposed.

A glass combustion-tube was then filled with copper oxide, and a current of ammonia passed until the whole was reduced. After complete removal of the water, the temperature was raised to 780°, when it was found that the percentage of ammonia decomposed in four experiments was 49·3, 42·6, 57·3, and 51·6, or, as a mean, 50·2. Of course in this case the amount of surface exposed was very large.

The results obtained may be summed up as follow:—

1. When ammonia-gas is passed through a porcelain tube, or an iron tube, or a glass tube filled with asbestos cardboard, the amount of decomposition at 500—520° is nearly equal and very small. It may be fairly assumed, therefore, that the temperature at which ammonia begins to decompose, under the most favourable circumstances, lies a little below 500°.

2. In contact with a glass surface, the temperature at which decomposition begins lies much higher.

3. The amount of decomposition depends partly on the rate of passage of the gas, or, in other words, on the time of exposure to heat.

4. The nature of the surface heated has an enormous influence on the extent of decomposition, as is shown by the difference between the effects of copper and of iron wire, and of glass and porcelain.

5. The extent of the surface also influences the amount of decomposition, as shown by the experiments with copper wire and reduced copper.

6. Attempts were also made to ascertain the influence of pressure and of time by heating ammonia to high temperatures in sealed glass tubes; but at the temperatures attained no decomposition ensued, while at the higher temperatures the tubes invariably burst, though protected by coiled copper wire, copper electrolytically deposited, and sheet copper. In one case, however, a glass tube containing ammonia was successfully heated to 780° or a little lower for six hours, without any appreciable decomposition of the gas.

It has been stated that in several cases the decomposition of the

ammonia was complete: this is, however, not strictly correct, since, although no ammonia could be recognised by volumetric analysis, even when a litre of mixed nitrogen and hydrogen was collected, yet the issuing gas had always a faint ammoniacal smell and an alkaline reaction sufficiently powerful to turn a piece of red litmus-paper blue.

In order to make quite certain of this point, an iron tube was heated to very bright redness with the blast, but even in this case the issuing gas contained a trace of ammonia.

From this result, together with Deville's observation that decomposition is never complete when the spark is passed, it appears certain that recombination of the nitrogen and hydrogen must take place, if only to a very minute extent; when, however, a mixture of dry nitrogen and hydrogen was passed through a red-hot glass tube containing iron filings, or through an iron tube, the presence of ammonia could not be recognised. When the mixed gases were moist, a trace of ammonia was formed, possibly due to the decomposition of water by iron and the formation of nascent hydrogen.

XV.—*On Camphoric Peroxide and Camphorate of Barium.*

By Charles T. Kingzett, F.I.C., F.C.S.

Some years ago, while engaged in the study of the peroxide obtained as a product of the air-oxidation of turpentine (*Chem. Soc. J.*, 1875, p. 213), I determined to repeat the experiments made by Brodie concerning the action of barium peroxide upon camphoric anhydride, with the view of comparing his product with mine; but unfortunately I was unable then to find sufficient time to complete this part of the investigation.

Brodie had stated (*Proc. Roy. Soc.*, **9**, 361, and **12**, 655; *Phil. Trans.*, 1863, p. 407; and *Chem. Soc. J.*, 1864, p. 266) that when camphoric anhydride is triturated with an equivalent quantity of hydrated barium peroxide in presence of ice-cold water, and the mixture is filtered, there is obtained a solution which is slightly alkaline (owing to the presence of a trace of dissolved protoxide of barium), and which, when rendered acid, exhibits the following properties: it bleaches indigo, oxidises ferrocyanide of potassium, and decomposes hydriodic acid; evolves oxygen on boiling, but fails to give a blue coloration with chromic acid, and does not discolour permanganate of

potassium; when the solution is evaporated to dryness, it leaves a residue containing camphoric acid.

Brodie analysed the solution as I shall now describe:—

1. A measured quantity was rendered acid, and titred by means of standard iodine solution.

2. To another measure carbonic acid solution was added, and the mixture was boiled, filtered, and then precipitated by sulphuric acid. (The addition of the carbonic acid effects the removal of baryta, which is invariably present through the decomposition of the barium peroxide.)

3. A third measure was precipitated with acetate of lead, and the precipitate was collected and weighed; it consisted of pure camphorate of lead.

Operating in this way Brodie obtained in two experiments the following results:—

Experiment I.

	At. wt.	Ratio calculated.	Ratio found.
$C_{10}H_{14}O_3$ =	182	25·12	25·12
O =	16	2·20	2·07
BaO =	153	21·12	21·51

Experiment II.

	Ratio calculated.	Found.	
$C_{10}H_{14}O_3$.....	21·43	21·43	
O.....	1·88	1·96	
BaO.....	18·00	17·88	mean of 16·54
			19·22
			2)35·76
			17·88

Brodie says it will be seen that this compound is a barium salt of the peroxide, and not a camphorate of BaO_2, by the fact that when treated with acids it does not yield peroxide of hydrogen, and that by the action of alkalis peroxide of barium is not reproduced. But do not Brodie's results admit of another interpretation? I think they do, and believe that when camphoric anhydride is triturated with water and barium peroxide, the anhydride is first converted by the addition of a molecule of water into camphoric acid, and that this product then decomposes the barium peroxide, producing camphorate of barium and peroxide of hydrogen. Such a product would exhibit most of the properties described by Brodie, and would of course give

the same results when analysed after his manner of proceeding. For whereas according to his view, the product has a composition which may be indicated thus:—

$$C_{10}H_{14}BaO_5 + H_2O,$$

according to my view it would have the composition—

$$C_{10}H_{14}BaO_4 + H_2O_2.$$

The experiments which I conducted in 1875 confirm my opinion, and in any case, now that I have called Brodie's views in question, they cannot be further accepted unless new proof of their correctness is forthcoming.

I will now generally describe the experiments I have referred to without entering into too great detail.

The camphoric anhydride I employed was prepared by distillation of camphoric acid, and re-sublimation of the product. The barium peroxide was prepared after the manner described by Brodie, viz., by dissolving the ordinary peroxide in dilute hydrochloric acid, and reprecipitating with baryta-solution. After removing the first portions of the precipitate containing oxides of iron, the further precipitate was washed with water, and finally dried by shaking it up with absolute alcohol, then isolating, and air-drying the purified product.

Experiment I.

Equivalent quantities of camphoric anhydride and peroxide of barium were placed in contact with ice-cold water in a well-stoppered bottle in a cool place, and the mixture was shaken from time to time. The pearly scales of peroxide gradually changed in appearance, and the whole bulk of solid matter was very much diminished. After several days the mixture was filtered, and upon examining the undissolved matter it proved to be entirely inorganic in character. The filtrate liberated iodine from iodide of potassium solution just as peroxide of hydrogen does. It was precipitated with dilute sulphuric acid and filtered, and the filtrate was concentrated by evaporation; during which process crystals separated. These, together with a further amount obtained on cooling, were collected, washed, and dried at 100°. Upon analysis the following results were obtained:—

0·3254 gram burnt with $PbCrO_4$ and metallic copper gave 0·693 gram CO_2 and 0·251 gram H_2O.

Percentages.	+ At. wt.		Theory per cent. of $C_{10}H_{16}O_4$.
C = 58·082	4·840 = 2·3	9·2	60
H = 8·604	8·604 = 4·1	16·0	8
O = 33·314	2·082 = 1·0	4·0	32

These results proved the crystals to consist of camphoric acid.

Experiment II.

This experiment was made to test the assertion of Brodie that the product of the action of barium peroxide upon camphoric anhydride does not yield peroxide of hydrogen with acids. A quantity of the two substances taken in molecular proportion was triturated together with ice-cold water, and then placed in a bottle, the mixture being shaken from time to time during four hours. The filtrate was treated with carbonic anhydride in excess to remove baryta, and the precipitated barium carbonate removed by filtration. The filtrate when tested was found to be exactly neutral. The barium was now removed by precipitation with dilute sulphuric acid. The filtrate gave with potassium iodide and starch the ordinary reactions exhibited by peroxide of hydrogen; with chromic acid it gave the characteristic blue coloration and evolution of oxygen peculiar to peroxide of hydrogen; and when it was added to permanganate of potassium, that solution was decolorised, and oxygen was evolved. These tests showed that peroxide of hydrogen was present in the solution.

Experiment III.

Barium peroxide and camphoric anhydride (2 grams and 4 grams respectively) were triturated with absolute alcohol, and the mixture was heated in a water-bath for one hour. The mixture was filtered hot. The filtrate was systematically examined, and found to contain only camphoric anhydride, which was obtained in a crystalline state upon concentration. The part undissolved by the alcohol was extracted with water. The watery extract was alkaline, but upon acidification with acetic acid a part of it was found to give the reactions of peroxide of hydrogen. The bulk of this aqueous solution was precipitated by alcohol, and the precipitate dried at 100°.

0·439 gram gave on ignition with sulphuric acid, 0·296 gram $BaSO_4$ = to 39·64 per cent. barium.

Camphorate of barium, ($C_{10}H_{14}BaO_4$), contains 40·89 per cent. barium, and $C_{10}H_{14}BaO_4,H_2O$ contains 38·81 per cent. barium. Doubtless the precipitate consisted of impure camphorate of barium.

Experiment IV.

2·25 grams pure $C_{10}H_{14}O_3$ and 8 grams pure hydrated BaO_2 were triturated with absolute alcohol, and the mixture subsequently digested at 100° for some time. The mixture on cooling was placed in a stoppered bottle and left at rest for several weeks. Then the mixture was filtered, and the undissolved part was treated with 50 c.c. water, which dissolved most of the mass, leaving only inorganic matter behind. Some alcohol was added to the aqueous solution, but not sufficient to cause a precipitate. Upon standing, the solution deposited fine needle-shaped and feathery crystals. These were collected, washed with absolute alcohol, and dried at 100°.

Analysis.

0·403 gram gave 0·2664 gram $BaSO_4$
0·3942 „ 0·486 „ CO_2
and 0·172 „ H_2O

Percentages.	÷ At. wt.	÷ Ba = 1.	
C = 33·62	2·801	9·89	$C_{10}H_{14}BaO_4,H_2O$,
H = 4·81	4·81	16·90	
Ba = 38·86	1·42	1·00	
O = 22·71	0·283	5·01	

which requires by theory—

Percentages.
C = 33·99
H = 4·53
Ba = 38·81
O = 22·66

This experiment was interesting, not merely as confirming the results of the previous observations, but also since by it camphorate of barium, crystallising with 1 mol. of water, was thus obtained for the first time. I can find no mention of such a hydrate having been previously met with, although analyses of the two following hydrates have been published, viz., the neutral salt, $2C_{10}H_{14}BaO_4,9H_2O$, and an acid salt, $(C_{10}H_{15}O_4)_2Ba,2H_2O$. Both these salts were obtained by boiling camphoric acid with excess of barium carbonate, and crystallisation of the solution (see *Watts's Dictionary*, **6**, First Supplement, p. 389).

Experiment V.

2 grams of pure $C_{10}H_{14}O_3$ and 6 grams BaO_2 (specially prepared) were triturated together with cold water, and the mixture, after stand-

ing and working together some time, was filtered. The filtrate was precipitated with alcohol, and the snow-white precipitate redissolved in water and reprecipitated with absolute alcohol, then washed and dried at 100°.

Upon analysis, 0·2866 gram ignited with H_2SO_4 gave 0·186 gram $BaSO_4$.

0·3732 gram gave 0·493 gram CO_2 and 0·179 gram H_2O.

Percentages.	÷ At. wt.	÷ Ba = 1.
C = 36·027	3·002	10·7
H = 5·329	5·329	19·1
Ba = 38·154	0·278	1·0
O = 20·490	1·280	4·6

If we now deduct the barium and re-calculate the percentages, we get—

Percentages.	÷ At. wt.		
C = 58·24	4·853	× 2	9·7
H = 8·61	8·61		17·2
O = 33·12	2·07		4·1

or $C_{10}H_{16}O_4$.

To sum up, it may be said that so far as these experiments go, they prove that the action of barium peroxide upon camphoric anhydride takes place only in the presence of water, and is of a secondary character, the anhydride first becoming camphoric acid by the assimilation of water, and this acid then decomposing the peroxide of barium, yielding camphorate of barium and peroxide of hydrogen. It is also proved that camphorate of barium containing 1 mol. of water may be obtained in a crystallised state.

Thus Brodie's idea as to the existence of a camphoric peroxide forming a compound with barium, of the formula $C_{10}H_{14}BaO_5$, is discredited.

Again, if it can be shown by experiment that camphoric acid decomposes barium peroxide just as sulphuric acid does, liberating peroxide of hydrogen, then it follows that Brodie has erroneously described the behaviour of the product towards chromic acid and permanganate of potassium, and equally that his theory of the production of camphoric peroxide by this process is entirely untenable. The simple experiments I have already described give the proof in question, but in order to confirm this by a more direct method, I have recently investigated the action of camphoric acid upon barium peroxide, and found that, as might be expected, it yields peroxide of hydrogen in presence of water. Since, then, camphoric anhydride is converted into camphoric acid by contact with water, it necessarily follows if barium peroxide be also present, that camphorate of barium

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and peroxide of hydrogen must represent the only possible products of such reactions, thus:—

$$C_{10}H_{14}O_3 + H_2O = C_{10}H_{16}O_4,$$
$$BaO_2 + C_{10}H_{16}O_4 = C_{10}H_{14}BaO_4 + H_2O_2,$$

and these are the only products that have been experimentally identified.

XVI.—*On the Influence of the Temperature of Distillation on the Composition of Coal-gas.*

By Lewis T. Wright, Assoc. Memb. I.C.E., &c.

The quantity of gas yielded by a certain weight of coal varies according to the applied temperature: with an increase of temperature the quantity of gas is increased and the illuminating power decreased.

The composition of the gas resulting from the application of various degrees of heat has not been very specially investigated, and this is perhaps the first systematic study of the variations in the composition of coal-gas produced by various temperatures of distillation.

In the following experiments no means were taken for the purpose of pyrometrically determining the temperatures employed; because, from the nature of the experiments, any degrees of temperature so arrived at, would, it is believed, have been illusory.

The variations of temperature in the first series are indicated by the variations in the volume of gas resulting from the distillation of equal weights of coal.

1st Series.

Some Newcastle coal was broken up and carefully mixed to ensure evenness of quality throughout the sample, from which different portions were to be taken for trial.

The coal was distilled in a small iron retort of the pattern usually employed for gas-coal testing. This retort was connected with a condenser, lime purifiers, and gasholder, and consequently the whole apparatus represented a gaswork in miniature. The charge of coal for which this apparatus is designed is $\frac{1}{1000}$ part of a ton, or 2·24 lbs., which quantity of coal can be thoroughly carbonised in periods varying from 25 to 45 minutes, according to the temperature employed and the description of coal.

It was arranged that four portions of 2·24 lbs. each of the broken and thoroughly mixed Newcastle coal should be distilled at various temperatures, ranging from a dull red heat to the highest heat attainable with an iron retort.

The manner in which these various temperatures were arrived at may be briefly described. The retort was heated to a dull red, and the first charge of coal carbonised; the fire was then increased, and the retort made perceptibly hotter, and the second charge of coal was carbonised; again the fire was increased, and the third charge of coal carbonised; and finally, when the fire had been so increased that the retort was at a bright orange heat, the last charge was carbonised.

The gas from each charge was of course separately collected and measured; the illuminating power was observed, and samples were drawn off for gas analysis.

The volumes obtained were reduced to 30-inch barometer and 60° F., saturated with water-vapour. The illuminating power is also corrected to a standard consumption of 5 cubic feet and 120 grains per hour.

The "candles per ton" in the following table are obtained by multiplying the yield of gas per ton of coals by the equivalent of 1 cubic foot in candles, or what is the same thing, multiplying the cubic feet per ton by the illuminating power, and dividing the result by 5.

	Gas per ton of coals.	Illuminating power.	Candles per ton.	
(1.)	8,250 cub. ft.	20·5 candles	33,950	1st charge.
(2.)	9,693 „	17·8 „	34,510	2nd „
(3.)	10,821 „	16·75 „	36,140	3rd „
(4.)	12,006 „	15·6 „	37,460	4th „

The four samples of coal-gas from the same coal distilled at various temperatures were analysed in a gas-analysis apparatus, somewhat approaching the Thomas type (*Chem. Soc. J.*, **35**, 231), and the following numbers were obtained:—

	(1.)	(2.)	(3.)	(4.)
H_2	38·09	43·77	—	48·02
CO	8·72	12·50	—	13·96
CH_4	42·72	34·50	—	30·70
C_nH_m	7·55	5·83	—	4·51
N_2	2·92	3·40	—	2·81
Carbon-density of $C H_m$	2·73	2·91	—	2·62

The analysis of the third sample for CO, CH_4, N_2, was lost, and un-

fortunately no further portion of this gas had been saved when this loss was discovered, but from the figures yielded by the combustion of the gas containing the absorbable hydrocarbons, it is evident that this sample occupied an intermediate place between 2 and 4.

Oxygen was always absent in the samples of gas collected, for precautions had been taken against any introduction of air during the process of distillation. A slight pressure, equal to about $\frac{1}{10}$ of an inch of water in the gasholder, was maintained during the experiments, and thus all parts of the apparatus were under a slight pressure.

It will be seen that, with increased temperature and consequently increased volume of gas produced from the same weight of coal, there is an increase in hydrogen and a decreased quantity of methane and other hydrocarbons. The carbon-density of these latter appears to increase, and then decrease with increased temperatures.

The following table gives the amount of each constituent in cubic feet per ton of coal yielded at the three different temperatures; and it will be observed that as the temperature of distillation is increased, more and more of the carbon and hydrogen in the coal is brought into the shape of permanent gas :—

Number of experiment.	Composition of gas.					Composition of hydrocarbons absorbed by SO_3.
	H_2.	CO.	CH_4.	C_nH_m.	N_2.	
1.....	38·09	8·72	42·72	7·55	2·92	C 2·73 H 3·84
2.....	43·77	12·50	34·50	5·83	3·40	C 2·91 H 4·12
3.....	—	—	—	—	—	—
4.....	48·02	13·96	30·70	4·51	2·81	C 2·62 H 5·76

Number of experiment.	Cubic feet of each constituent yielded by 1 ton of coal.					Carbon vapour per 100 vols. of gas.	Ratio carbon vapour. Illuminating power.
	H_2.	CO.	CH_4.	C_nH_m.	N_2.		
1.....	3142·4	719·4	3524·4	622·9	240·9	72·08	3·51
2.....	4242·6	1211·6	3344·1	565·1	329·6	63·93	3·59
3.	—	—	—	—	—	60·66	3·62
4.....	5765·3	1676·0	3685·8	541 5	337·4	56·49	3·62

There is much that is inexplicable in the connection between the percentage volume of the C_nH_m hydrocarbons and the photogenic power of coal-gas; and it was known long ago that there is no direct pro-

portionality between the two. Some years ago a method of determining the photogenic power of coal-gas by analysis was worked out in a manner (first perhaps conceived by the illustrious Dr. Henry) somewhat as follows:—The percentage volume of hydrocarbons absorbable by chlorine or bromine was determined, also the specific gravity of the gas before and after the absorption of the hydrocarbons (other than methane). By these means the specific gravity of the absorbable hydrocarbons was arrived at, and it was found that by multiplying the percentage volume of the C_nH_m into their specific gravity in a state of vapour as they existed in the gas, a number was obtained agreeing very closely with the photogenic power as determined by candles with the photometer. Of course for so empirical a method to have yielded such results is more of an accident than anything else.

The influence of such neutral gases as carbonic anhydride and nitrogen is better understood. These gases have a deleterious influence proportional to their specific heats, as I pointed out in 1876 (*Journal of Gas Lighting*, vol. 30), and as was demonstrated by Rossetti *Gazzetta chimica italiana*, **7**, 422; *Chem. Soc. J.*, 1878, Abstr., 467). The influence of such gases as methane, carbonic oxide, and hydrogen, in spite of the researches of Frankland and Thorne, is not quite clear. It is evident that methane is a more useful constituent than hydrogen or carbonic oxide. Frankland and Thorne found that benzene-vapour yielded 5·3 per cent. more light when diluted with carbonic oxide than with hydrogen; but the method of photometry employed in that research does not make it quite clear whether the result can be accepted as approximating very closely to the truth.

Gases of different illuminating power, *consumed at different rates* in a fish-tail burner, can hardly be expected to yield results having much relation to a common standard. For instance, their benzolised hydrogen was burned at the rate of 4·95 cubic feet, and had an illuminating power corrected to the 5-feet standard of 28·58 candles. It is fair to assume that with any other rate of consumption the illuminating power corrected to 5 feet would have been different.

The benzolised carbonic oxide was consumed at the rate of 4·22 cubic feet per hour, and when corrected to the 5 cubic feet standard, the illuminating power was 23·48 candles. Had the benzolised carbonic oxide been consumed at 4·95 cubic feet per hour, as was the benzolised hydrogen, the illuminating power corrected to 5 feet would have been different.

Some experiments I made a few years ago would indicate that carbonic oxide is a greater diluent of luminosity than hydrogen. Trials were made for the purpose of ascertaining how many volumes of carbonic anhydride, nitrogen, air, carbonic oxide, and hydrogen

respectively, would completely disilluminate 100 vols. of coal-gas (17 candles) by previous admixture. By disillumination is meant the disappearance of any white luminosity in the flame, which was burned from a jet, and was therefore symmetrical in shape.

The results obtained are tabulated below.

100 *Volumes Coal-gas required for Disillumination.*

Luminosity recoverable by previous heating of mixture	196	parts	air.
	196	„	N_2.
	100	„	CO_2.
Luminosity not so recoverable	627	„	CO.
	1233	„	H_2.

It does not necessarily follow from these results that the illuminating power of a luminous gas would be effected equally by admixture with carbonic oxide or hydrogen (in quantities considerably short of what is required for total disillumination) in the proportion of 627 to 1233 respectively.

These experiments of mine are somewhat confirmed by those recently made by Dr. Percy Frankland (p. 30 of this volume), an abstract of which has appeared in some of the papers. From this I gather that he found ethylene to yield more luminosity in hydrogen than in carbonic oxide. It must not be forgotten that illuminating power is an arbitrary and variable standard. By using different burners and rates of consumption, widely different results can be obtained, and in experiments of this kind it is highly desirable that the conditions of experiment should be as fair for one gas as for another.

From the researches of Landolt, Hilgard, Blochmann and others, it would appear that hydrogen and methane disappear on combustion more rapidly than carbonic oxide. It seems difficult, with our present knowledge of the subject, to come to any precise conclusions as to the relative value of carbonic oxide and hydrogen in coal-gas, though it would be easy to mix coal-gas of known candle power with small quantities of CO and H_2, and observe the loss of candle power.

I hope soon to have an opportunity of making some experiments in this direction.

On looking over the numbers obtained by the analysis of the four samples of gas, I found a simple relation between the illuminating power and the carbon, which is expressed in the table under the ratio

$$\frac{\text{Carbon vapour}}{\text{Illuminating power}}.$$

2nd Series.

Many years ago Dr. Henry studied the composition of the gas coming off the coal at various stages of the distillation. I do not know where his original memoir may be found, but the following table is taken from *Chemical Technology*, 2nd ed., vol. 1, part ii, page 581: Ronald and Richardson, 1855.

Time of collection.	Specific gravity.	Absorbed by chlorine	Light carburetted hydrogen	Carbonic oxide	Hydrogen	Nitrogen
		Out of 100 parts of gas from Wigan cannel coal.				
1st hour	0·6·0	13	82·5	3·2	0	1·3
	0·620	12	72	1·9	8·8	5·3
	0·630	12	58	12·3	16	1·7
5—10 hours after commencement	0·500	7	56	11	21·3	4·7
	0·345	0	20	10	60	10

The following experiments are in the same direction as those of Dr. Henry. The samples were taken off clay retorts distilling Newcastle coal in the ordinary process of gas-making; but precautions were observed to prevent access of air into the retort or gas collected, by ensuring that the gas was being distilled and the samples collected under a slight pressure. Under these circumstances I have always failed to find any trace of oxygen in the gas. The samples were taken from the ascension pipe connected with the retort, and therefore contained the usual impurities of crude coal-gas. Before passing the portions of the samples for analysis into the measuring tube, the trace of ammonia was always removed by dilute sulphuric acid.

In the practice of gas making, a red-hot retort, on being first charged with coal, suffers a considerable reduction of temperature, owing to the mass of cold coal suddenly thrown in, and the early portions of gas distilled off are therefore not submitted to the action of a very high temperature; but as the coal becomes more and more carbonised, and the retort has less work to do, the heat gains on the coal, the portion near to the sides of the retort being perhaps red-hot, and consequently the latter portions of gas have to suffer the disintegrating action of a much higher temperature than the early portions. Thus, the gas collected at various stages of the distillation might be expected to exhibit variations in composition somewhat similar to those yielded by the same coal distilled at various temperatures.

I have tabulated the results obtained from three different retorts

working under slightly different conditions as regards temperature and weight of coal.

1st Case.

Samples collected from a clay retort which was charged with a quantity of coal requiring six hours for complete distillation.

	Time after commencement of distillation.		
	40 minutes.	3 hours.	5 hours 45 minutes.
H_2S	0·40	0·78	0·38
CO_2	2·08	1·34	0·59
H_2	25·36	48·36	71·94
CO	4·52	6·73	7·52
CH_4	56·46	37·46	14·61
C_nH_m	8·81	3·13*	2·78
N_2	2·37	2·20	2·18
	100·00	100·00	100·00

* Carbon density of C_nH_m.... 3·2

2nd Case.

The retort in this case was charged with a quantity of coal expected to be completely distilled in four hours. The retort was, however, under charged, as the sample drawn off 2 hours 45 minutes after commencement suggests, and was considerably hotter than in the first case.

	Time after commencement of distillation.	
	30 minutes.	2 hours 45 minutes.
H_2S	1·31	1·38
CO_2	1·52	
H_2	41·68	68·51
CO	4·33	8·49
CH_4	43·65	19·45
C_nH_m	6·01	0·84
N_2	1·50	1·33

3rd Case.

Retort charged with a quantity of coal requiring six hours for distillation :—

	Time after commencement of distillation.			
	10 minutes.	1 hour 30 minutes.	3 hours 25 minutes.	5 hours 35 minutes.
H_2S	1·30	1·42	0·49	0·11
CO_2	2·21	2·09	1·49	1·50
H_2	20·10	38·33	52·68	67·12
CO	6·19	5·68	6·21	6·12
CH_4	57·38	44·03	33·54	22·58
C_nH_m	10·62	5·98	3·04	1·79
N_2	2·20	2·47	2·55	0·78
	100·00	100·00	100·00	100·00
Carbon density of C_nH_m	2·86	3·1	3·38	2·29

The second series yields results generally in accord with those obtained by Dr. Henry, and with some published by Prechtl in 1835. As the distillation proceeds, the hydrogen rapidly increases, whilst the methane decreases. In the third case the carbonic oxide is very regular in amount; though in the first and second cases the carbonic oxide increases towards the end of the distillation, the decrease in hydrocarbons absorbable by SO_3 is very marked, and from the numbers obtained in the third case it would appear that their carbon density rises and then falls as the distillation proceeds.

XVII.—*Researches on Secondary and Tertiary Azo-Compounds.* No. II.

By Raphael Meldola.

In the previous communication on this subject (*Chem. Soc. J.*, 1883, Trans., **1**, 25), the action of diazotised paranitraniline upon primary and secondary monamines was investigated, and the secondary and tertiary azo-bodies obtained from the resulting compounds were described. I have now the pleasure of laying before the Society the results of the extension of these experiments to tertiary monamines.

ACTION OF DIAZOTISED PARANITRANILINE UPON TERTIARY MONAMINES.

I. *Action upon Dimethylaniline.*

An aqueous solution of diazoparanitrobenzene chloride was gradually mixed with a well-cooled solution of 1 mol. of dimethylaniline hydrochloride. The mixture becomes bright red, and after standing for some hours a copious deposit of scaly crystals with a beautiful steel-blue reflection is formed. The crystals were collected, washed with cold water, and dissolved in boiling dilute hydrochloric acid, and the deep red solution was filtered. On cooling, the filtrate deposited large needles, with a splendid metallic blue reflection, consisting of the hydrochloride $NO_2.C_6H_4.N_2.C_6H_4.N(CH_3)_2,HCl$.

Paranitrobenzene-azodimethylaniline.—The free base, liberated from its salt by the action of ammonia, was obtained as a chocolate-brown powder, dissolving with difficulty in boiling alcohol with a brown colour, and separating from the solution on cooling in reddish-brown microscopic needles fusing at 229—230°.

The platinum salt was obtained as a reddish granular precipitate by adding a solution of $PtCl_4$ to an alcoholic solution of the hydrochloride and washing with alcohol containing hydrochloric acid:—

0·2165 gram gave 0·0446 gram Pt.

	Theory for $2\left[C_6H_4<^{NO_2}_{N_2.C_6H_4.N(CH_3)_2.HCl}\right]PtCl_4$.	Found.
Pt.	20·72 per cent.	20·60

In addition to the properties already described, the base dissolves in strong sulphuric acid with an orange colour, becoming red on dilution. It is soluble also in benzene and glacial acetic acid, the solutions being orange. It crystallises from acetic acid in lustrous scales.

Paraamidobenzene-azodimethylaniline, $C_6H_4<^{1\,NH_2}_{4\,N=N.4\,C_6H_4.\underbrace{N(CH_3)_2}_{1}}$.

—The base was reduced by warming its alcoholic solution with ammonium sulphide, the reduction being indicated by the change of colour of the solution from brown to yellow. On mixing with water, a bright orange precipitate separated, which was purified by washing, solution in dilute hydrochloric acid, filtration, and reprecipitation by ammonia. The amido-base was finally obtained by crystallisation from dilute alcohol in the form of small brick-red needles, having a faint metallic shimmer, and fusing at 182—183°. By adding $PtCl_4$ to an aqueous solution of the hydrochloride, a double platinum salt

separated in the form of a brown bulky precipitate, consisting of microscopic needles:—

0·1526 gram gave 0·0458 gram Pt.

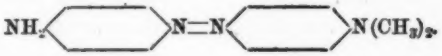
	Theory for $\left[C_6H_4<\begin{matrix}NH_2\\N_2.C_6H_4.N(CH_3)_2\end{matrix}\right]_2HCl.PtCl_4$.	Found.
Pt.	30·25 per cent.	30·11

The base is insoluble in boiling water, but dissolves readily in most of the ordinary solvents with a yellow colour. The salts are easily soluble in water, forming red solutions. On adding weak acids, such as acetic or oxalic, to an alcoholic solution, a green colour is produced, which changes to red on dilution with water. A green colour is also developed when a few drops of hydrochloric acid are added to the alcoholic solution, but this colour is only transitory in the case of the mineral acids, the solution rapidly becoming red. These colour-changes are doubtless associated with the formation of monacid and biacid salts. The substance dissolves in strong sulphuric acid with an orange colour. When it is heated with methyl alcohol and excess of methyl iodide in a sealed tube to 100° for 3—4 hours, an extremely insoluble methiodide crystallising in brown scales is formed. Boiled with acetic anhydride, it furnishes an acetyl-derivative, crystallising from alcohol in tufts of small orange needles melting at 217°. Heated with aniline and aniline hydrochloride, it gives a violet colouring matter, resembling the redder shades of induline, and no doubt related to the colouring matters of this class. The amido-group of this base is readily diazotised by the action of nitrous acid, and a solution of the diazo-salt exhibits a most striking reaction when made extremely dilute and exposed to the air. Under these circumstances a splendid blue colour is developed,* especially when the solution is made neutral or slightly alkaline by the addition of one or two drops of ammonia; the colour thus formed slowly disappears on standing, and a brown flocculent substance separates out.

Complete Reduction of the Base.—A solution of the base in dilute hydrochloric acid was treated with zinc-dust till completely decolorised, and the excess of zinc was then removed by filtration. The presence of dimethylparaphenylene-diamine in the solution was proved by the Lauth reaction in the following way:—The filtrate was saturated with

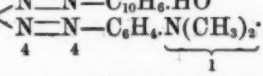
* This property renders the substance a most delicate test for nitrous acid. It possesses the advantage over metaphenylene-diamine that the solutions of its salts can be kept for an indefinite time without undergoing alteration, and at the same time the colour developed (blue) is much more satisfactory when only a trace of nitrite is present than the brown produced by metaphenylene-diamine. I have obtained by this test distinct indications of 1 part $NaNO_2$ in 64,000 parts of water, and this is probably considerably above the lowest limit of its delicacy.

hydrogen sulphide, and a solution of ferric chloride added till the odour of the gas had disappeared. On adding excess of zinc chloride solution and filtering, there remained on the filter the zinc double salt of Caro's so-called "methylene blue," recognisable by its intense colouring power and the well-known property of dyeing wool from a bath made alkaline with ammonia. Since this colour is produced only by dimethyl*para*phenylene-diamine, the constitution of the base may be written :—*



SECONDARY AZO-COMPOUNDS, $Ph—N{=}N—C_6H_4—N{=}N—C_6H_4.(CH_3)_2$.

β-Naphtholparaazobenzene-azodimethylaniline,



A solution of the amido-base in dilute hydrochloric acid was diazotised by adding the theoretical quantity of sodium nitrite. No perceptible change of colour occurred, but on pouring the liquid into a well-cooled solution of β-naphthol in sodium hydroxide, a dark brown precipitate was formed, and this when collected, washed, and dried, was obtained in the form of a dull bronzy powder. In order to purify this crude secondary azo-compound, it was dissolved in boiling alcoholic soda, and the solution filtered into cold water. The compound thus precipitated was collected, washed with water, dried, and crystallised from glacial acetic acid and toluene successively. The pure compound was thus obtained in the form of bronzy green glistening needles melting at 209—210°.

I. 0·2989 gram gave 0·7959 gram CO_2, and 0·1401 gram H_2O.
II. 0·1512 „ „ 22·8 c.c. N at 16·6°, and 754·4 mm. bar. = 0·02632 gram N.

* It is of interest to mark the relationship of this body to the dimethylanilineazyline obtained by Lippmann and Tleisner (*Ber.*, 1882, 2136) by the action of N_2O_2 upon dimethylaniline :—

$H_2N—C_6H_4—N{=}N—C_6H_4—N(CH_3)_2$.
Paramidobenzene-azodimethylaniline.

$(CH_3)_2N—C_6H_3{=}N—N{=}C_6H_3—N(CH_3)_2$.
Dimethylanilineazyline.

	Theory for $C_{24}H_{21}N_5O$.	Found. I.	Found. II.
C	72·91	72·62	—
H	5·21	5·21	—
N	17·72	—	17·41

This secondary azo-body is but slightly soluble in boiling alcohol, more readily in hot glacial acetic acid, benzene, toluene, and chloroform. Its solutions are of a deep red colour. It is freely dissolved by alcoholic potash with a red colour. Hydrochloric acid added to the alcoholic solution gives a fine blue coloration. The solution in strong sulphuric acid is green, becoming blue on dilution, then violet, and finally brown, and precipitating.

It is interesting to note that the diazotised amido-base does not form secondary azo-compounds with any of the sulphonic acids of β-naphthol.

α-Naphtholparaazobenzene-azodimethylaniline,

$$C_6H_4\begin{cases}{}^{1}N{=}{}^{a}N{-}C_{10}H_6.{}^{a}HO \\ {}^{4}N{=}{}^{4}N{-}C_6H_4.\underbrace{N(CH_3)_2}_{1}.\end{cases}$$

—This compound was prepared in the same manner as the foregoing, and was obtained as an uncrystallisable bronzy powder by deposition from a hot toluene solution. It closely resembles the β-naphthol compound in most of its properties, dissolving but slightly in alcohol, and more readily in the hydrocarbons of the benzene series. The solutions are red, the alcoholic solution becoming blue on addition of hydrochloric acid. The colour-reaction with strong sulphuric acid is the same as that given by the β-compound. The solution in alcoholic potash or ammonia is violet instead of red, as in the case of the β-compound. At a temperature of about 200° the substance froths up and decomposes.

Resorcinolparaazobenzene-azodimethylaniline,

$$C_6H_4\begin{cases}{}^{1}N{=}{}^{4}N.C_6H_3.{}^{3}HO.{}^{1}HO \\ {}^{4}N{=}{}^{4}N.C_6H_4.\underbrace{N(CH_3)_2}_{1}\text{'}\end{cases}$$

was obtained as a brown gelatinous precipitate, drying to a brown powder. It dissolves but sparingly in boiling alcohol with a reddish-orange colour, which changes to violet on adding a few drops of hydrochloric acid, and then to blue on further addition of acid. It dissolves slightly in glacial acetic acid, the solution being red when hot, and violet when cold. It is almost insoluble in toluene, this solvent becoming only slightly coloured of an orange tint when boiled with the substance. It dissolves in hot aqueous solutions of the caustic alkalis

with a red, and in alcoholic potash with a reddish-violet colour. It imparts a violet colour to strong sulphuric acid, this colour changing to blue on dilution. It decomposes when heated like the α-naphthol compound.

Phenolparaazobenzene-azodimethylaniline,

$$C_6H_4\begin{cases}{}^{1}N{=}{}^{4}N.C_6H_4.{}^{1}HO \\ {}^{4}N{=}{}^{4}N.C_6H_4.\underbrace{N(CH_3)_2}_{1}\end{cases}'$$

forms a brown powder, dissolving in aqueous solution of potassium or sodium hydroxide with a rich brown colour, and with a red colour in an alcoholic solution of these alkalis. In all other respects its properties are similar to those of the resorcinol compound.

II. Action of Diazoparanitrobenzene upon Ethyldiphenylamine.

On mixing the aqueous solution of diazoparanitrobenzene chloride (1 mol.) with an alcoholic solution of ethyldiphenylamine (1 mol.), a deep red colour is produced, and a viscid bronzy tar separates out. This tarry mass solidified on standing, but the nitroazo-compound could not be obtained pure by crystallisation, so the mass was dissolved in hot alcohol, and at once reduced by cohobation with ammonia and ammonium sulphide. The reduction of the nitro-group is indicated by the change of colour of the solution from orange to yellow, and on pouring it into strong brine, the amidoAzo-compound separates as a dark tarry substance, also uncrystallisable. The salts of the amido-base, $NH_2.C_6H_4.N_2.C_6H_4.N.C_6H_5.C_2H_5$, dissolve in water with a fine red colour, and can be readily diazotised by the action of nitrous acid. The diazo-salts exhibit the same blue coloration on neutralisation and exposure to the air, as the corresponding compound from dimethylaniline, but the reaction is not so striking as in the case of the latter tertiary amine. On mixing a solution of the diazotised amido-base with an alkaline solution of β-naphthol, a brown precipitate was obtained, which, after being collected and washed, dried to a dull bronzy uncrystallisable powder.

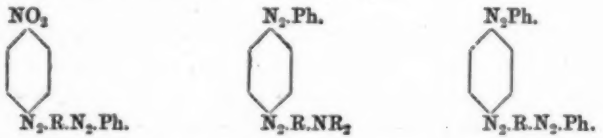
β-Naphthol-paraazobenzene-azoethyldiphenylamine,

$$C_6H_4\begin{cases}{}^{1}N{=}N.C_{10}H_6.{}^{\beta}HO \\ {}^{4}N{=}N.C_6H_4.N.C_2H_5.C_6H_5\end{cases}'$$

is readily soluble with a red colour in alcoholic potash, and is dissolved also by alcohol and the benzene hydrocarbons with a similar colour. The alcoholic solution becomes blue on adding hydrochloric acid. It dissolves in strong sulphuric acid, with a dull indigo-blue, becoming bright blue on dilution.

The uncrystallisable nature of the foregoing compounds, and the tendency to give rise to the formation of tarry impurities at every stage, renders these reactions much less satisfactory than in the case of dimethylaniline.

The azo-compounds thus far described being all derived from paranitraniline, the substituting azo-groups and their linked radicles necessarily occupy the positions 1 : 4.



It appeared of interest, therefore, to extend the reactions to the isomeric nitranilines and their homologues, in order to be able to compare the properties of a corresponding series of compounds containing the azo-groups, &c., in a different position. The following experiments were made with metanitraniline :—

Action of Diazotised Metanitraniline upon Primary Monamines.

I. *Action upon Aniline.*

As will be seen on reference to the previous paper (*Chem. Soc. J.*, Nov., 1883, Trans., p. 428), *para*nitraniline when diazotised gives the most satisfactory results with *meta*-monamines of the C_nH_{2n-6} series. Some preliminary experiments with diazometanitrobenzene served to show that in this case there was but little difference in the yield of nitroamidoazo-compound with aniline or metaxylidine respectively. The product is small in both cases, so for the sake of simplicity aniline was employed.

On mixing well-cooled aqueous solutions of metanitrodiazobenzene chloride* and aniline hydrochloride (1 mol. of each), a brown precipitate of the diazo-compound $NO_2.C_6H_4.N_2.NH.C_6H_5$ separates in the course of about an hour. On standing for six hours, the brown precipitate becomes orange-coloured and crystalline, indicating its transformation into the isomeric azo-compound. This transformation is, however, always incomplete, and the azo-compound was invariably found to be contaminated with a certain quantity of the diazo-body.

Metanitroazoamidobenzene, $\underset{1}{NO_2}.C_6H_4.\underset{3}{N}=\underset{4}{N}.C_6H_4.\underset{1}{NH_2}$, was obtained

* The precautions given in the last paper (p. 428) with respect to the diazotising of the nitraniline also apply here. The formation of dinitrodiazoamidobenzene by the action of nitrous acid upon metanitraniline has been proved in Victor Meyer's laboratory by Hallman (*Ber.*, 1876, 390).

by crystallisation from dilute alcohol in the form of beautiful orange-coloured fern-like leaflets having a faint violet reflection. It is insoluble in water and dilute acids, but dissolves readily with a yellow colour in alcohol, acetone, and benzene. The platinochloride,

$$2(NO_2.C_6H_4.N_2.C_6H_4.NH_2.HCl).PtCl_4,$$

was obtained as a brick-red powder on adding a solution of $PtCl_4$ to a solution of the base in alcohol and hydrochloric acid. The salts of the base do not separate from an alcoholic solution on the addition of mineral acids. The melting point could not be determined with precision, but it lies near 210°, at which temperature the substance undergoes a considerable darkening and becomes almost black.

An attempt to reduce the nitro-group revealed a striking contrast between the behaviour of this body and the corresponding series of para-compounds. A freshly precipitated specimen of the nitroamidoazo-compound was cohobated with ammonia and ammonium sulphide for about 14 hours, at the end of which time a certain portion of the substance appeared to be unacted upon. This was removed by filtration, and the solution was acidulated with hydrochloric acid and evaporated to a small bulk. The sulphur was filtered off, and the filtrate on neutralisation furnished a small quantity of some flocculent substance, but nothing of the nature of a diamidoazo-base. A further examination of the filtrate showed that it contained meta- and para-diamidobenzene. It thus appears that in the meta-series of nitroamidazo-compounds both the nitro-group and the diazo-group are attacked simultaneously by ammonium sulphide,* a result which, as will be seen later on, is confirmed by the behaviour of the corresponding α-naphthylamine compound.

Metanitroazobenzene-azo-β-naphthol,

$$\underset{1}{NO_2}.C_6H_4.\underset{3}{N}=\underset{4}{N}.C_6H_4.\underset{1}{N}=\underset{\alpha}{N}.C_{10}H_6.\underset{\beta}{HO}.$$

The nitroazo-base was diazotised in alcoholic solution in the usual way, and filtered into an alkaline solution containing 1 mol. of β-naphthol. A brick-red precipitate was obtained, which was collected and washed, and then dissolved in alcoholic soda and precipitated by an acid. After being washed and dried, the substance was dissolved in boiling toluene, and thus obtained in the form of warty concretions of microscopic orange crystals with a glistening green metallic reflection. The yield of this secondary nitroazo-compound is extremely small. The substance is but slightly soluble in alcohol, more readily in glacial acetic acid and toluene; its solutions are of an orange colour. It dissolves readily in alcoholic soda with a violet

* In an alcoholic solution the decomposition by ammonium sulphide is complete and rapid.

colour. The solution in strong sulphuric acid is green, becoming blue on dilution. The melting point is about 217—218°.

II. *Action of Metanitrodiazobenzene upon α-Naphthylamine.*

On mixing aqueous solutions of the diazo-chloride and α-naphthylamine hydrochloride (1 mol. of each), the contents of the beaker become semi-solid, from the formation of a bulky gelatinous precipitate. The latter was filtered off, well washed with water, basified by ammonia, and the red base was dissolved in boiling alcohol. On adding hydrochloric acid to the orange alcoholic solution, the colour changes to a beautiful red, and the hydrochloride of the nitroamidoazo-compound separates out in the form of a bronzy-green crystalline precipitate, which under the microscope is seen to consist of short needles.

Metanitrobenzene-azoamido-α-naphthalene,

$$\underset{1}{NO_2}.C_6H_4.\underset{3}{N}=\underset{\alpha}{N}.C_{10}H_6.\underset{\alpha}{NH_2},$$

was obtained by crystallisation from toluene in the form of dark brown microscopic needles having a glistening metallic reflection, and appearing garnet-red by transmitted light. When crystallised rapidly, so as to obtain very fine crystals such as result from the rapid cooling of the dilute alcoholic solution, the substance appears of a bright red colour. The fusing point is 202—203°. It dissolves freely in cold acetone with an orange colour. The solutions in benzene and toluene are yellowish-orange, and the acetic acid solution red. It dissolves in strong sulphuric acid with a very red shade of violet, which becomes a true red on dilution.

In order to submit the base to the action of sulphide of ammonium, it was obtained in a semi-gelatinous state by stirring the alcoholic solution into a large bulk of cold water. Some of the base thus prepared was left for about 24 hours in contact with ammonium sulphide in the cold, but no reduction had taken place. On warming the contents of the flask, the substance gradually passed into solution. After about four hours, the solution was cooled, and a small quantity of some flocculent bye-product that had separated out was removed by filtration. The filtrate contained no trace of any diamidoazo-body, so that here, as in the case of the aniline compound, both the nitro- and the diazo-groups are attacked by the reducing agent. The nitroamidoazo-compound is completely decomposed also when the cold alcoholic solution is mixed with sulphide of ammonium, and allowed to stand for 3—4 hours.

Metanitrobenzene-azo-α-naphthalene-azo-β-naphthol,

$$\underset{1}{NO_2}.C_6H_4.\underset{3}{N}=\underset{\alpha}{N}.C_{10}H_6.\underset{\alpha}{N}=\underset{\alpha}{N}.C_{10}H_6.\underset{\beta}{HO}.$$

The amido-group in the nitroamido-azo-compound,

$$C_6H_4\begin{cases}{}^{1}NO_2 \\ {}^{3}N_2.C_{10}H_6.NH_2,\ {}^{\alpha}\end{cases}$$

could be diazotised, though with difficulty, by proceeding in the following manner:—

A solution of the base in alcohol was mixed with a small quantity of the theoretical amount of sodium nitrate dissolved in water, and HCl added to the well-cooled solution till it showed a decided acid reaction. After being left at rest for about half an hour, a further quantity of the $NaNO_2$ solution and more HCl was added, and the mixture again allowed to stand for half an hour. The nitrite and acid were thus added alternately at the intervals stated till the whole of the theoretical quantity had been mixed in, and the yellowish solution of the tetrazo-chloride was then filtered into an alkaline solution of β-naphthol. The dark reddish gelatinous precipitate thus formed was collected, washed thoroughly with water, and purified by crystallisation, first from hot aniline, and then from boiling toluene. The pure compound was thus obtained in the form of a felted mass of fibrous microscopic needles, having a dull bronzy appearance. At a temperature of 245° the substance blackens and decomposes.

I. 0·1726 gram gave 0·4417 gram CO_2 and 0·0649 gram H_2O.
II. 0·2095 gram gave 28 c.c. N at 16·5° and 763·76 mm. bar. = 0·0327 gram N.

	Theory for $C_{26}H_{18}N_6O_3$.	Found. I.	Found. II.
C.....	69·64	69·79	—
H.....	4·02	4·17	—
N.....	15·62	—	15·65

This secondary nitroazo-compound is almost insoluble in boiling alcohol or glacial acetic acid. It dissolves in chloroform and hot aniline with a violet colour. The toluene solution is red when hot and reddish-violet when cold. It dissolves in boiling alcoholic soda or potash with a blue colour. In strong sulphuric acid the substance dissolves with a dark olive colour, which on dilution becomes blue and finally violet.

The diazotised nitroamidoazo-compound gives with alkaline solutions of the sulphonic acids (mono- and di-) of β-naphthol a small yield of violet secondary nitroazo-sulphonic acids, having no tinctorial value.

The nitro-group in the secondary nitroazo-compound appears to be reduced by adding ammonium sulphide to a solution of the substance

in alcoholic potash. On adding the reducing agent to the cold blue solution the colour changes to red, and a reddish gelatinous precipitate at once separates. This precipitate apparently consists of the amido-compound, $NH_2.C_6H_4.N{=}N.C_{10}H_6.N{=}N.C_{10}O_6.HO$, but as it was not found possible to diazotise the amido-group this body was not further investigated.

Metanitrobenzene-azo-α-naphthalene-azo-α-naphthol,

$$NO_2.C_6H_4.N{=}N.C_{10}H_6.N{=}N.C_{10}H_6.HO,$$

was obtained as a dark uncrystallisable powder insoluble in alcohol, but dissolving with a red colour in toluene, chloroform, and glacial acetic acid. In strong sulphuric acid it gives a dark indigo-blue coloration, which on dilution becomes bright blue, and finally violet when the substance is precipitated. It dissolves in alcoholic potash with a greenish-blue colour. Heated in the dry state the substance froths up and decomposes.

Metanitrobenzene-azo-α-naphthalene-azoresorcinol,

$$NO_2.C_6H_4.N{=}N.C_{10}H_6.N{=}N.C_6H_3.HO.HO.$$

On mixing the solution of the tetrazo-chloride and an alkaline solution of resorcinol, a brown gelatinous precipitate at once separates. The substance when dry forms a bronzy powder, slightly soluble in boiling alcohol with a reddish colour, and somewhat more soluble in glacial acetic acid, toluene, and chloroform with an orange colour. It separates from its solutions when cold in a flocculent state. It is to some extent soluble with a blue colour in boiling aqueous alkalis, and freely soluble with a similar colour in alcoholic potash. It dissolves with a green colour in strong sulphuric acid, this colour changing to bluish-green, and the substance precipitating on dilution. When heated in a dry tube it swells up and decomposes.

III. *Action of Metanitrodiazobenzene upon β-Naphthylamine.*

The aqueous solutions of the diazo-chloride and amine salt were mixed in the usual way, and the bright orange precipitate which immediately formed was collected and washed. After crystallisation from dilute alcohol, it was obtained in the form of magnificent orange-coloured needles, melting at 177°. This substance dissolves in alcohol, acetic acid, acetone, chloroform, toluene, &c., with an orange colour. The acetone and alcoholic solutions become red on the addition of hydrochloric acid, but the salts do not separate out. It dissolves with a fine violet colour in strong sulphuric acid.

I. 0·3105 gram gave 0·7446 gram CO_2 and 0·1193 gram H_2O.

II. 0·2631 gram gave 42 c.c. N at 13° and 766·6 mm. bar. = 0·050 gram N.

	Theory for $C_{16}H_{12}N_4O_2$.	Found. I.	Found. II.
C.....	65·75 per cent.	65·40	—
H.....	4·11 „	4·27	—
N.....	19·18 „	—	19·02

When acted upon by nitrous acid, this substance, like the corresponding para-compound (*Chem. Soc. J.*, 1883, Trans., p. 436),* furnishes a nitroso-derivative. These β-naphthylamine compounds, in this property of forming nitroso-derivatives, as well as in their splendidly crystalline character, the solubility of their salts in alcohol, and their low melting points as compared with the corresponding α compounds, appear to differ widely from the true nitroamidoazo-bodies. I am inclined to believe that this difference is the result of a different constitution, arising most probably from the interaction of the diazo- and amido-groups which occupy the ortho-position with respect to one another. This view receives a certain amount of support from the fact that the ortho-diamines under the action of nitrous acid do not yield bodies of the triamidoazobenzene type, but the contiguous ortho-groups appear to interact with formation of azimido-compounds of the type of Ladenburg's so-called "amidoazo-phenylene," $C_6H_4\langle\begin{matrix}N\\|\\N\end{matrix}\rangle NH$ (*Ber.*, 1876, p. 219).† A similar view with respect to the constitution of the azo-β-naphthol compounds has been recently advanced by Liebermann (*Ber.*, 1883, p. 2158), and my own investigations have led to the same conclusion respecting the constitution of the azo-β-naphthylamine derivatives. These researches are not yet completed, but I hope to be able to make a detailed study of the nitroso and other derivatives, and the reduction-products of these bodies. The facility with which the bodies in question furnish nitroso-derivatives can be explained only on the view that a replaceable imido-hydrogen is present, or else that the nitroso-group enters the naphthalene residue. Whichever of these views may eventually prove to be correct, the fact that these compounds cannot be diazo-

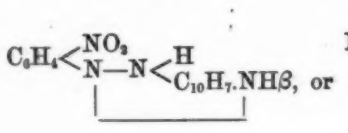
* In the previous paper no C and H determination was given, and I here subjoin the results of the combustion of a specimen of pure paranitrobenzene-azoamido-β-naphthalene:—

0·1261 gram gave 0·3026 gram CO_2 and 0·0472 gram H_2O.

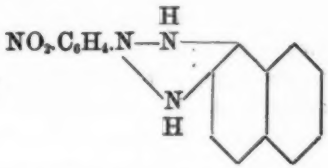
Theory for $C_{16}H_{12}N_4O_2$, C, 65·75 per cent.; H, 4·11 per cent. Found: C, 65·44 per cent.; H, 4·15 per cent.

† This constitutional formula is assigned by Griess (*Ber.*, 1882, p. 1878).

tised, combined with the circumstance that nitrous acid readily converts them into nitroso-bodies, points distinctly to the conclusion that *an amido-group is no longer present.* In view of these considerations, and bearing in mind, as an important link in the chain of evidence, that the compound from metanitraniline and α-naphthylamine has been shown in the course of the present paper to contain an amido-group, I would suggest the following constitutional formula for the azo-derivatives of β-naphthylamine as a modification of that given in my last paper (*loc. cit.*, p. 431):—



, or



I hope shortly to be in a position to lay before the Society further experimental evidence bearing upon this question.

Action of Diazotised Metanitraniline upon Secondary and Tertiary Monamines.

Metanitrobenzene-azodiphenylamine, $NO_2.C_6H_4.N{=}N.C_6H_4.NH.C_6H_5$ (1, 3, 4, 1).

—An aqueous solution of metanitrodiazobenzene chloride (1 mol.) was gradually mixed with an alcoholic solution (1 mol.) of diphenylamine, and the well-cooled mixture allowed to stand for 2—3 hours. A red colour is immediately developed on mixing the solutions, and a brown precipitate soon settles out. The latter on being collected and washed becomes of an orange colour. The substance was purified by two or three crystallisations from dilute alcohol, and was thus obtained in the form of reddish-brown scales glistening with a slight metallic reflection. The melting point is 136—137°.

0·2718 gram gave 0·6758 gram CO_2 and 0·1055 gram H_2O.

	Theory for $C_{18}H_{14}N_4O_2$.	Found.
C.....	67·92	67·81
H.....	4·40	4·31

This azo-compound is soluble in alcohol, acetone, glacial acetic acid, benzene, &c., with an orange colour. The solutions in the benzene hydrocarbons are somewhat yellower than those in the other solvents. On adding hydrochloric acid to the alcoholic solution, an orange-red colour is developed, and this passes into a magenta-like

red as the acid is gradually increased. If the alcoholic solution is concentrated the addition of hydrochloric acid causes the immediate separation of the hydrochloride of the base in the form of a brown gelatinous precipitate. All the salts of this base are very unstable, and are at once decomposed by contact with water. A very unstable double platinum salt is precipitated in the form of microscopic reddish-brown needles when platinic chloride solution is added to the alcoholic solution of the hydrochloride. This salt could not be washed without decomposition, and the platinum could not therefore be determined. The base dissolves in strong sulphuric acid with a fine violet colour. On adding sodium nitrite to the cold solution of the substance in glacial acetic acid the colour gradually changes to yellow, and yellow scaly crystals begin to separate out. On diluting with water an orange-coloured crystalline nitroso-compound was obtained, which after crystallisation from alcohol, formed warty clusters of short orange needles melting at about 127—128°.*

The reduction of this azo-compound by means of ammonium sulphide in alcoholic solution does not give rise to the formation of an amidoazo-base, but a reddish tarry substance containing sulphur compounds, and having a most disagreeable odour, is produced.† By complete reduction in alcoholic solution with zinc-dust and hydrochloric acid, a solution is obtained which on exposure to the air gradually becomes blue, and on the addition of ferric chloride a fine blue colouring-matter is immediately precipitated. The complete reduction of the azo-compound thus produces a mixture of para-amidodiphenylamine and metaphenylenediamine in equal numbers of molecules, and this mixture on oxidation gives rise to an unstable blue colouring-matter, which in all probability belongs to the type of Witt's "tolulylene blue" (*Chem. Soc. J.*, 1879, Trans., p. 356):—

$$C_6H_4\!<\!\begin{matrix}NH.C_6H_5\\ N\end{matrix} + C_6H_3.NH.NH_2 + 2O = C_6H_4\!<\!\begin{matrix}NH.C_6H_5\\ N.C_6H_3.NH.NH_2\end{matrix} + 2H_2O.$$

(H_2 and H H are removed; the blue colouring matter is the product.)

These blue colouring-matters are, as shown in a paper recently

* The corresponding nitroso-compound, prepared in a similar manner from *para*-nitrobenzene-azodiphenylamine, was obtained by crystallisation from benzene in the form of brown scaly crystals, which begin to soften at 161°, and fuse completely at 169—170°. I propose to continue the investigation of these and other nitroso-derivatives of the azo-compounds.

† My friend Dr. O. N. Witt informs me that he has prepared an azo-compound from diphenylamine and a new nitrotoluidine of the formula $CH_3 : NH_2 : NO_2 = 1 : 2 : 4$. The body, on reduction by ammonium sulphide, also fails to give an amidoazo-base.

published by Nietzki (*Ber.*, 1883, p. 464), closely related to the compounds of the saffranine series.

Metanitrobenzene-azodimethylaniline, $NO_2.C_6H_4.N{=}N.C_6H_4.N(CH_3)_2$ (1, 3, 4, 1).

—Metanitraniline hydrochloride was diazotised in the usual way, and mixed with the theoretical quantity of dimethylaniline hydrochloride dissolved in water. The mixed solution becomes red, and on leaving the mixture at rest for twelve hours, a deep reddish-brown precipitate forms. The latter was collected and washed with water till it had become bright orange, this change of colour indicating the decomposition of the hydrochloride of the new nitro-azo-compound by water, and the liberation of the free base. The substance was purified by crystallisation from hot dilute hydrochloric acid (about equal parts of strong hydrochloric acid and water), from which the hydrochloride separates on cooling in the form of red microscopic needles. After being washed and basified, the substance was finally crystallised from dilute alcohol, and thus obtained as a bright reddish-orange microcrystalline powder melting at 157—158°.

0·4270 gram gave 0·9747 gram CO_2 and 0·1996 gram H_2O.

	Theory for $C_6H_4{<}^{NO_2}_{N_2.C_6H_4.N(CH_3)_2}$.	Found.
C.....	62·22 per cent.	62·25
H.....	5·18 „	5·19

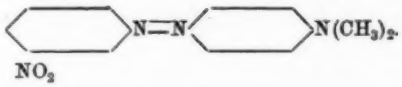
. The substance dissolves in the ordinary solvents, such as alcohol, benzene, acetone, acetic acid, &c., with a yellowish-orange colour. The solution in strong sulphuric acid is pale orange, becoming red on dilution with water. By the action of ammonium sulphide upon the alcoholic solution no satisfactory reduction-product was obtained.

In order to determine the constitution of this body, complete reduction of a specimen dissolved in dilute hydrochloric acid was effected by means of zinc-dust, and the colourless solution thus obtained was tested for metaphenylenediamine and paradimethyldiamidobenzene. On adding Fe_2Cl_6 solution a blue colouring-matter is formed, which is no doubt the lower homologue of Witt's "toluylene blue.

$$C_6H_4{<}^{N(CH_3)_2}_{N}{}^{H_2} + C_6H_3.NH.NH_2 + 2O = C_6H_4{<}^{N(CH_3)_2}_{N.C_6H_3.NH.NH_2}{}^{H\ H} + 2H_2O.$$

Another portion of the solution treated with Fe_2Cl_6 in presence of sulphuretted hydrogen gave a considerable quantity of "methylene

blue." It thus appears that the position of the NO_2-group with respect to the azo-group has no effect upon the position which the latter occupies in entering the dimethylaniline residue, and the constitutional formula of the new compound is—



As compared with the corresponding series of compounds derived from paranitraniline, the azo-bodies derived from metanitraniline are characterised by greater instability, as shown by the readiness with which the molecule becomes severed at the N_2-group under the action of ammonium sulphide, thus precluding the possibility of preparing tertiary azo-bodies by this method. The compounds of the meta-series are likewise more soluble in all solvents, and have lower melting points than the para-compounds, as shown in the following table:—

Formula.	Para-series.	Meta-series.
$C_6H_4<^{NO_2}_{N_2.C_{10}H_7.NH_2\alpha}$	252°	202—203°
$C_6H_4<^{NO_2}_{N-N<^{H}_{C_{10}H_7.NH\beta}}$ ...	180	177
$C_6H_4<^{NO_2}_{N_2.C_6H_4.N<^{H}_{C_6H_5}}$	151	136–137
$C_6H_4<^{NO_2}_{N_2.C_6H_4.N(CH_3)_2}$	229—230	157—158

From this table it will be seen also that the difference between the melting points of the β-naphthylamine compounds is far less than between any other pair of isomerides, a fact which gives additional support to the view that these bodies are differently constituted to the true azo-compounds.

The present investigations have been conducted in the laboratory of the Atlas Works, and I have great satisfaction in again being able to acknowledge my obligations to Messrs. Brooke, Simpson, and Spiller. The extension of these researches to the ortho-series, and to the action of the diazotised nitranilines, &c., upon the phenols will form the subject of future communications to the Society.

XVIII.—*Note on the Nitrogenous Matters in Grass and Ensilage from Grass.*

By Edward Kinch, Royal Agricultural College, Cirencester.

That grass and other fodder crops, like most crude vegetable products, contain nitrogenous matters other than albuminoïds, is well known, also that the amount of these matters depends largely on the relative stage of development of the plant, the less mature plants containing a larger percentage of non-albuminoïd nitrogen: but it is still common, in expressing the results of analyses, to represent the whole of the nitrogen as existing in the form of albuminoïds. Our knowledge of the nature of these nitrogenous matters is yet very imperfect. Ammonia and nitric acid have been detected in some cases, and possibly in some cases alkaloïds and peptones, but the principal part of the non-albuminoïd nitrogen of grass appears to exist in the form of amides and amido-acids.

O. Kellner (*Bied. Centr.*, 1879, 270; *Chem. Centr.*, 1879, **10**, 744 and 761; *C. J.*, 1879, Abstr., 819) has determined the amount of non-albuminoïd nitrogen in many specimens of grass and other fodder plants at different stages of growth, the soluble albuminoïds being in most cases precipitated by lead acetate. Of the total nitrogen in the crops from 7·5 to 38·5 per cent. was found to be non-albuminoïd, the higher amounts being, especially in the case of the grasses, in the younger plants.

Peter Collier, in his report to the Commissioner of Agriculture for 1880 (*Rept. of Commis. Agriculture*, 1880, Washington), gives the results of the examination of 15 grasses and three leguminous plants, each at from three to six different stages of growth, and of 37 separate specimens of grasses mostly in full flower. In these analyses the albuminoïds were determined by Stützer's method (*J. f. Landwirthsch.*, 1880) after treatment with water containing a little lactic acid, and precipitation of the dissolved albuminoïds with copper hydrate.

In the great majority of cases the non-albuminoïd nitrogen constituted between 6 and 40 per cent. of the total; in a few cases it was lower; in one case none was present, and in two cases it rose to 50 per cent. of the total nitrogen.

H. P. Armsby (*Rept. Connecticut Expt. Stat.*, 1879) determined the non-albuminoïd nitrogen in 21 samples of fodder, by various processes; its amount was from 8·9 to 39·6 per cent. of the total nitrogen.

The results of other experimenters are in accordance with these. In the examination of several specimens of the principal plants of the hill pastures of Scotland, including not only grasses, but *Cyperaceæ*, *Juncaceæ*, &c., I have found that usually from 10 to 33 per cent. of the nitrogen is non-albuminoïd.

What may be the exact nutritive value of these non-albuminoïd nitrogenous bodies is as yet unknown, but it is certain that the amido-compounds can replace albuminoïds in food to a limited extent only.

Certain amides, as asparagin, can to a certain extent prevent waste of albuminoïds by preventing their oxidation; but cannot entirely supersede them. See Weiske and others (*Zeitschr. f. Biologie*, **15**, 261, and **17**, 415).

Whether, during the fermentations to which grass and other fodder crops are subjected in order to produce ensilage, the albuminoïds which they contain undergo any change into other nitrogenous bodies not having the physiological functions of albuminoïds, and to what extent such changes occur, is a matter not only of much scientific interest, but of great practical importance in considering the economic relations of ensilage. This point has been hitherto unnoticed in published analyses of ensilage, although it seems very likely such changes would occur during the processes, in some respects allied to digestion, to which the fodder is subjected. As a small preliminary contribution, I record analyses of a sample of grass and of the ensilage made therefrom.

The sample of grass was taken from that being filled into a silo, after passing through a chaff-cutting machine, on the farm of Mr. T. R. Hulbert, North Cerney, Gloucestershire, on July 17th, 1883, the silo was filled and closed a few days later.

The grass was coarse, and contained a good deal of miscellaneous herbage, notably thistles and *Ranunculi*. The sample of ensilage was taken from the same part of the silo to which the grass was filled, on December 8th, 1883. The ensilage was not under great pressure, the weight placed on the surface being only about 50 lbs. per square foot. The ensilage when taken out was brown, scarcely acid, and with very slight odour, but after a very short time it began to smell strongly of acetic acid; after some hours, however, this smell disappeared and was replaced by the odour of butyric acid, which was noticeable throughout the homestead in which the ensilage was in use. The ensilage mixed with dry fodder was readily eaten by cattle.

The results of the analyses in percentages are as follows:—

	In fresh substances.		In dry matter.	
	Grass.	Ensilage.	Grass.	Ensilage.
Water, lost at 100° C.	76·93	74·99	—	—
Ether extract	1·27	1·78	5·55	7·12
Total N × 6·25	2·15	2·36	9·32	9·44
Fibre	6·65	7·98	28·82	31·89
Ash	1·96	2·52	8·50	10·10
Soluble carbohydrates, &c., by difference	11·04	10·37	47·81	41·45
	100·00	100·00	100·00	100·00
Albuminoïds by phenol method ...	1·95	1·06	8·46	4·25
Albuminoïds by copper hydrate method	1·98	1·11	8·57	4·46
Albuminoïds by mercuric hydrate..	—	1·14	—	4·55
Albuminoïds by lead hydrate	—	1·18	—	4·72
Per cent. of total nitrogen which is non-albuminoïd, by phenol method	—	—	9·2	54·9

The amount of free acid is not given above; it varied very much with exposure; after exposure for a short time the total amount was found to be equivalent to 0·87 per cent. of acetic acid. The fresh ensilage distilled with water gave only 0·03 per cent. of volatile acid, as acetic acid.

The method referred to as the phenol method is Church's process, consisting in the estimation of the nitrogen, after precipitating all the albuminoïds, with a little metaphosphoric acid and a hot 4 per cent. solution of carbolic acid. In the copper hydrate method, a modification of Ritthausen's, the soluble albuminoïds were precipitated by heating to boiling with recently prepared copper hydrate. In the ensilage the soluble albuminoïds were also precipitated with mercuric chloride and a very slight excess of potassium hydroxide, and with lead acetate and potassium hydroxide, aided by heat. These two methods may be supposed to precipitate any bodies of the nature of peptones, if such were present; they gave slightly higher results than the other methods. The results with the copper hydrate method, with grasses, I have invariably found to be slightly higher than those by the phenol method, possibly owing to the presence of some acid containing nitrogen and forming an insoluble compound with the copper hydrate. All care was taken in collecting and sampling the specimens, and if we assume that they were strictly comparable, though it is difficult to get such specimens with such material, then judging from the amount of ash, there has been a loss of about 18 per cent. of combustible constituents, with a slight loss of water. The

percentage of ether extract has increased, as has always been noticed before in ensilage, sometimes in part owing to the formation of lactic acid. The amount of soluble carbohydrates has decreased through fermentation, and has not been reinforced to the full extent by alteration in the fibre, which consequently has slightly increased in percentage. Such changes are exactly in accord with analyses of clover-hay and ensilage by Dr. A. Voelcker, quoted in the *Field* of January 20, 1883, and of sainfoin and its ensilage by Weiske and of others.

But the most striking change is in the condition of the nitrogenous matters; in the grass only 9 per cent. of the nitrogen is non-albuminoïd, and in the ensilage nearly 55 per cent., reckoned from the albuminoïds by the phenol method. The increase in the percentage of total nitrogen in the ensilage was about one-half only of the increase in percentage of ash, indicating that a loss of nitrogen may have taken place.

The only published analyses bearing on this point are some in which the soluble nitrogenous matter, considered, however, simply as albuminoïds, and the insoluble nitrogenous matter were determined separately. Voelcker, quoted in the *Times*, March 21, 1883, found 57 per cent. of the nitrogenous matter of rye ensilage soluble in water, and 40 per cent. of the nitrogen of maize ensilage.

Sutton (*Field*, February 10, 1883, *Chem. News*, **47**, 287) gives two analyses of hay and two of ensilage made from the same two grasses. In these cases the fermentation had apparently not proceeded to the same length, or, perhaps, in the same direction, as in the ensilage above mentioned, for the percentage of ash was not higher in the ensilage, and the soluble carbohydrates had increased, whilst the indigestible fibre had decreased; but here again the soluble nitrogenous matter had increased from 12 per cent. in the hay to 53 and nearly 60 per cent. in the ensilage. Doubtless the whole of the soluble nitrogenous matter in these cases was not albuminoïd.

Whether such changes in the nitrogenous matter always take place in ensilage, or, as is likely to a less extent when the fodder is subjected to greater pressure, and what exact forms of nitrogenous bodies are produced (only traces of ammonia were found in this case), and whether and to what extent the albuminoïds are lost as food are points requiring investigation; I hope ere long to be able to throw light on some of them.

University of

XIX.—*On the Expansion of Liquids.*

By D. Mendelejeff, Foreign Member of the Chemical Society.

(Translated from the Russian by B. Brauner.)

Though every liquid has its own peculiar coefficient of expansion, it has long been a *desideratum* (as may be seen for example from abstracts published in the *Fortschritte der Physik* since 1845) to find a general expression for the expansion of all liquids. The generalisation which I now lay before the Society is connected with the discussion of this question which has already taken place, and with the additional experimental material which has been collected by chemists, chiefly for the purpose of studying the specific volumes of liquids at their boiling temperatures. The present paper is, however, limited to the discussion of the physical side of the question of the expansion of liquids. At some future time I may direct attention to the history of the subject, and to the consideration of the connection between the expansion of liquids, their composition, and other properties.

From all that we know about the expansion of liquids (Pierre, Kopp, Thorpe, Elsässer, and others) we can now easily see that the change of volume V with increase of temperature, t, takes place uniformly and regularly for liquids of different composition and properties, but the usual empirical formula

$$V = 1 + At + Bt^2 + Ct^3 + \ldots\ldots\ldots \quad (I)$$

by which the connection between V and t is represented, does not allow a direct conclusion of this kind to be drawn. To make this clear, the adjoining table has been drawn up containing the data* for the expansion of the 47 liquids studied by Thorpe (*Chem. Soc. J.*, 1880, Trans., 141, 327); they are arranged in the order of increase of expansion, and show distinctly the regularity and quantitative uniformity in the expansion of liquids of the most different natures.

* For PBr_3 and AsF_3 Thorpe's experimental data were recalculated by me, and in the table are given numbers following from my calculations, whereas for all other bodies numbers are given, following from Thorpe's own interpolation (formula I). According to Thorpe's calculations, the volumes of PBr_3 at 10°, 30°, 60°, 100°, and 150° = 1·0085, 1·0258, 1·0528, 1·0914, and 1·1448. Their accordance with the formula given below (K = 0·000841) is still greater than in the case of numbers recalculated by me. Thorpe's data for PBr_3 agree very closely with those of Pierre, and this allows the greater confidence to be put in the numbers referring to this liquid.

	10°.	30°.	60°.	100°.	150°.
$PC_6H_5Cl_2$	1·0083	1·0250	1·0507	1·0869	1·1368
PBr_3	1·0085	1·0259	1·0530	1·0916	1·1450
$NC_6H_5H_2$, aniline	1·0087	1·0262	1·0535	1·0925	1·1473
$SO_2(OH)Cl$	1·0091	1·0273	1·0552	1·0941	1·1465
C_2H_5Cl	1·0095	1·0285	1·0578	1·0994	1·1585
S_2Cl_2	1·0094	1·0285	1·0584	1·1016	1·1618
$CHBr_3$	1·0094	1·0287	1·0584	1·1012	—
ICl*	1·0093	1·0283	1·0586	1·1027	—
C_2H_4ICl	1·0094	1·0286	1·0587	1·1023	—
$(CH_2Br)_2$	1·0096	1·0293	1·0605	1·1061	—
$S_2O_5Cl_2$	1·0098	1·0299	1·0616	1·1074	—
CrO_2Cl_2	1·0097	1·0298	1·0618	1·1086	—
$VOCl_3$	1·0097	1·0298	1·0618	1·1087	—
$TiCl_4$	1·0099	1·0301	1·0619	1·1084	—
NC_6H_7, picoline	1·0098	1·0299	1·0620	1·1097	—
$POBrCl_2$	1·0101	1·0307	1·0630	1·1098	—
$AsCl_3$	1·0100	1·0306	1·0631	1·1104	—
$PSCl_3$	1·0102	1·0310	1·0639	1·1121	—
C_3H_5OCl, epichlorhydrin	1·0103	1·0315	1·0653	1·1155	—
C_3H_5OH, allyl alcohol	1·0103	1·0314	1·0660	1·1204	—
$P(C_2H_5O)Cl_2$†	1·0104	1·0324	1·0680	1·1204	—
C_2Cl_3OCl	1·0110	1·0332	1·0682	1·1201	—
$CBrCl_3$	1·0109	1·0332	1·0686	1·1206	—
$POCl_3$	1·0109	1·0333	1·0693	1·1232	—
$C(NO_2)Cl_3$	1·0111	1·0337	1·0694	1·1226	—
Br_2	1·0108	1·0335	1·0698	—	—
C_2Cl_3OH	1·0111	1·0347	1·0719	—	—
$SnCl_4$	1·0117	1·0356	1·0736	1·1302	—
CH_2ClCH_2Cl	1·0116	1·0356	1·0742	—	—
CS_2	1·0116	1·0360	—	—	—
C_8H_{18}‡	1·0119	1·0360	1·0745	1·1331	—
$SOCl_2$	1·0117	1·0360	1·0752	—	—
PCl_3	1·0117	1·0360	1·0755	—	—
C_8H_{18}§	1·0120	1·0368	1·0771	1·1401	—
CCl_4	1·0121	1·0372	1·0778	—	—
C_7H_{16}‖	1·0122	1·0376	1·0792	1·1439	—
SO_2Cl_2	1·0124	1·0381	1·0797	—	—
C_7H_{16}¶	1·0125	1·0386	1·0815	—	—
$CHCl_3$	1·0125	1·0387	1·0818	—	—
NC_3H_5, propionitril	1·0125	1·0388	1·0820	1·1479	—
CH_3CHCl_2	1·0130	1·0404	1·0855	—	—
CH_2Cl_2	1·0134	1·0417	—	—	—
$SiCl_4$	1·0136	1·0425	1·0904	—	—
AsF_3	1·0144	1·0433	1·0885	—	—
$CO(CH_3)_2$, acetone	1·0138	1·0433	1·0920	—	—
C_2H_3OCl	1·0139	1·0433	—	—	—
$(NO_2)_2$	1·0157	—	—	—	—

* For a body like iodine monochloride, we can assume with De Heen, that it begins to dissociate on heating already when liquid, sooner than it distils.

† $PCl_3 + C_2H_5OH = HCl + P(C_2H_5O)Cl_2$.

‡ Octane from methyl-hexyl-carbinol, boiling at 125·46°, sp. gr. at 0° = 0·71883.

§ Diisobutyl, boiling at 108·5 °, sp. gr. at 0° = 0·71110.

‖ From *Pinus sabiniana*, boiling at 98·4°, sp. gr. at 0° = 0·70048.

¶ Ethyl-amyl, boiling at 90·3°, sp. gr. at 0° = 0·69692.

That there is a uniformity in the expansion of liquids may be inferred, not only from an arrangement of a similar kind, but also from the mutual comparison of the expansion of liquids. Compare for example the expansion of mercury with that of two liquids which are placed very far from each other in the table. We have, according to Thorpe, for phosphorus tribromide :

t =	10°	20°	30°	40°
V =	1·00847	1·01706	1·02577	1·03463

For mercury we have the following empirical expression, which was calculated by myself from Regnault's experimental data (*Russ. Chem. Phys. Soc. Jour.*, 1875) :

$$V = 1 + 0{\cdot}0001801T + 0{\cdot}00000002T^2.$$

According to this formula the same volumes as those given for PBr_3 correspond with the temperatures :

	T = 46·8°	93·7°	140·9°	189·1°
and	T : t = 4·68	4·68	4·69	4·72

In exactly the same way we have for nitrogen tetroxide :

t	= 5°	10°	15°	20°
V	= 1·00789	1·01573	1·02370	1·03196
T	= 43·6°	86·5°	129·7°	174·6°
T : t	= 8·72	8·65	8·65	8·70

From this follows that phosphorus tribromide expands 4·7 times, and nitrogen tetroxide 8·7 times more strongly than mercury, but in qualitative respect the expansion of these, as well as of other liquids, is uniform.

The uniformity in the expansion of liquids shown above may be represented by the formula :

$$V = (1 + \frac{k}{n}t)^n$$

which, according to Gay-Lussac's law, represents the uniformity in the expansion of gases. For gases, $n = +1$; for liquids we must assume $n = -1$.*

* The formula $V = e^{at}$, which has been several times proposed as the expression of the expansion of liquids, though it answers pretty satisfactorily to the observed uniformity in the expansion of liquids, does not agree with the reality. Thus for example, I find for phosphorus tribromide, from Thorpe's data, that at $t = 40°$, $a = 0{\cdot}000851$; for $t = 80°$, $a = 0{\cdot}000866$; for $t = 120°$, $a = 0{\cdot}000885$; for $t = 160°$, $a = 0{\cdot}000907$; but this shows that the volume of the liquid increases more rapidly with increasing temperature than should follow from the formula $V = e^{at}$.

The expression given above for liquids will therefore take the following form:—

$$V = (1-kt)^{-1} = \frac{1}{1-kt} \quad \text{II.}$$

But, as the specific gravities are inversely proportional to the volumes, it follows that if D represents the density at $t°$ and D_0 that at 0°, we shall have:

$$D = D_0 (1-kt) = D_0 - k D_0 t \quad \text{III.}$$

This requires the change of density with changing temperature, $\frac{dD}{dt}$ to be a constant $= -kD_0$.

In my recent investigation (*Russ. Chem. Phys. Soc. Jour.*, 1880—1883) of the products of distillation of Baku petroleum, I was often obliged to determine in different portions of the distillate the change of density with changing temperature, viz., $\frac{dD}{dt}$, and I found that it always remains very nearly constant* within wide limits of temperature, this being in accordance with III. I have further to remark that, as far back as 1860 (*Liebig's Annalen*, **114**, 165), I found that the coefficient of change of density $\frac{dD}{dt}$ varies with changing composition, more simply than the coefficient of expansion of liquids with relation to volume, $\frac{dV}{dt}$. These circumstances have induced me to consider the expansion of all liquids in this sense, and the first result of this comparison is in accordance with the simple expression† of

If we expand this formula, we obtain the series $V = 1 + at + \frac{1}{2}a^2t^2 + \frac{1}{3}a^3t^3 + \ldots$ As a rule, in the empirical formula $V = 1 + At + Bt^2 + Ct^3 + \ldots$ the value $B > \frac{1}{2}A^2$ and $C > \frac{1}{3}A^3$.

* Miss E. K. Gutkowska has determined (1881) in my laboratory the specific gravity of American kerosine (petroleum), and found it: at 0° = 0·8056; at 16° = 0·7940; at 32° = 0·7824; at 48° = 0·7708; from which $\frac{dD}{dt} = -\frac{0·0116}{16} = -0·000725$. For Baku petroleum, $D_0 = 0·8278$, and $\frac{dD}{dt} = -0·000760$. For Ragosine machine oil, No. 1, $D_0 = 0·9131$, and $\frac{dD}{dt} = -0·000633$. For the products of distillation of Baku petroleum, the coefficients of alteration of specific gravity kD_0, were published by me in the *Russ. Phys. Chem. Soc. Jour.*, 1883, p. 189—192.

† I will omit, that already after the year 1840, attempts were made to find a general law for the expansion of liquids, and to express it with relation to the coefficient of alteration of specific gravity. If I am not mistaken, the first attempt was made by Wilhelmi, but I have tried in vain to find out this forgotten investigation. Meanwhile it appears that Groshans, in 1853, Watterson Potter, in 1863, and

the expansion of liquids according to formula II. The applicability of this formula may be shown by a few examples.

The expansion of phosphorus tribromide, according to Thorpe's data, is represented empirically as follows:—

t =	40°	60°	80°	100°	120°	140°
V =	1·0348	1·0530	1·0720	1·0916	1·1123	1·1340

and, assuming $k = 0{\cdot}000341$, we obtain, according to formula II:

V =	1·0348	1·0531	1·0721	1·0918	1·1123	1·1335

Let us take another instance from a number of highly expansible liquids (Thorpe) like silicon tetrachloride. For this Thorpe gives:

t =	10°	20°	30°	40°	50°
V =	1·0136	1·0278	1·0425	1·0579	1·0738

Assuming in formula II $k = 0{\cdot}001360$, we obtain:

V =	1·0138	1·0280	1·0425	1·0575	1·0730

This and other examples show that formula II is in accordance with experiments up to ten thousandths of the volume; but in determining the expansion itself errors may be assumed to have occurred, especially as regards very small fractions of volume, as indeed may be seen, not so much by comparing together the investigations of one and the same author, but rather from a comparison of the data of two different authors with reference to one and the same liquid. Thus for example Kopp gives at 100° for aniline the volume 1·0915, and Thorpe 1·0925; for silicon tetrachloride Pierre gives at 50° (of the mercury thermometer) 1·0753, and Thorpe for 50° (of the air thermometer) 1·0738 (this reduced to mercury thermometer = 1·0735), &c.

If we assume for k, in formula II, the real values below, we have the following volumes:—

	10°.	30°.	60°.	100°.	150°.
$k = 0{\cdot}0009$	1·0091	1·0277	1·0571	1·0989	1·1561
$k = 0{\cdot}0010$	1·0101	1·0309	1·0638	1·1111	1·1765
$k = 0{\cdot}0011$	1·0111	1·0341	1·0707	1·1236	1·1976

For the upper part of the foregoing table these numbers correspond with the expansion of real liquids according to Thorpe's investigations. So $k = 0{\cdot}0010$ nearly represents the expansion of $AsCl_3$ and

others (see *Fortschritte der Physik*), proposed to express the expansion of liquids by a formula similar to II. Evidently, then, the subject was at that time of interest to scientific men, but it has in the meantime been forgotten, and renewed investigations are required to call attention to it.

of $PSCl_3$. In all the above bodies investigated by Thorpe, the value of k varies from 0·00080 to 0·00155.

But just as for gases, the expression $V = 1 + kt$ applies only to a first approximation, or to a so-called ideal gas, so does the expression $V = (1-kt)^{-1}$ apply for liquids only to a first approximation, namely, ideal liquids.* Real gases and liquids show deviations to the one side or to the other from the above-mentioned expressions of expansion. These deviations are not large in either case (they are of the same order as regards k and V), and, as may be expected, they are especially remarkable near temperatures at which the state of the bodies changes. Thus vapours, as is well known, exhibit at temperatures near the boiling points of their respective liquids rates of expansion different from those which belong to them at greater distances from the temperatures at which they are converted into liquids. In like manner liquids near their boiling temperatures show an apparent change of the coefficient of expansion.† Phosphorus tribromide, for example, for which $k = 0{\cdot}000841$, exhibits near its boiling point (173°) a rate of expansion greater than that which is calculated from formula II. At 160°, for example, the volume 1·1562 is found, instead of 1·555, as calculated from II. The experimental data for liquids near their temperatures of solidification, are not numerous enough to enable us to say with confidence that near the temperatures at which they pass into the solid state, their coefficient of expansion is always changed; still cases are known in which such a change is insignificant. Thus it has recently been shown by Beilby (*Chem. Soc. J.*, 1883, Trans., 338), for paraffin melting at 38°, that liquid paraffin shows, from 38° to 60°, a perfectly constant change of specific gravity, namely, $\frac{dD}{dt} = -0{\cdot}000727$. This constancy proves that in this case the expansion of paraffin already follows formula III.

In the case of actual liquids, the deviation from the ideal form of expansion, as far as can be judged from known cases—other conditions remaining constant—increases not only as the liquid approaches

* According to my opinion, an ideal liquid, as a basis of kinetic theory of liquids, is characterised in reference to the action of heat by two signs: firstly, for such a liquid, $V = (1-kt)^{-1}$, or from this, $\frac{dV}{dt} = kV^2$, or $\frac{dD}{dt} = -kD_0$; and secondly, for it $a^2 = a^2_0(1-k_1t)$ in which a^2 is the capillary constant at $t°$, a^2_0 at 0°, from which follows $\frac{da^2}{dt} = -a^2_0k_1$. This last expression is founded upon experiments of Gay-Lussac, Brunner, Frankenheim, my own, De Heen, and of others.

† A subject for further experimental investigation would be the solution of the question, in what manner and how much the expansion of volatile liquids is changed at different pressures. I should like to submit this theoretically important question to an experimental solution (see my paper in *Liebig's Annalen*, 109, 1).

the point at which its state of aggregation is changed, but also with diminishing density, increasing cohesion (the value a^2), and diminishing molecular weight, or, what is the same, with diminishing vapour-density.* So in the case of two isomeric liquids (*e.g.*, aniline and picoline, or CH_2ClCH_2Cl and CH_3CHCl_2 from Thorpe's data), the molecular weight is the same, and the deviations (as well as the numeric value of k) increase with diminishing specific gravity. Exactly as water, amongst common liquids, possesses the smallest molecular weight, its freezing and boiling temperatures being at the same time very near each other, whereas the capillary constant which expresses its cohesion is very great, so, it seems to me, that by these circumstances the well-known deviations in the expansion of water are satisfactorily accounted for. About 50° the value k for water approaches 0·00047; about 25—30° it is one and a half times smaller, whereas at 100° it is one and a half times greater than this value. No other liquid hitherto well studied shows an equally rapid change of expansion. Besides, I think, that the study of the expansion of aqueous solutions, and the development of Grassi's investigations (*Ann. Chim. Phys.* [3], **31**, 437) on the compressibility of water (it diminishes with increase of k, whereas in the case of other liquids it increases) and of aqueous solutions, will be able to throw some light upon the exceptional and singular deviations (from II and III) in expansions shown by water. As regards the deviations of real liquids from the ideal form of expansion, I would observe in the first place, that the value of the deviation is, as a rule, numerically small, and that it has a different sign for different liquids, similar for example to the deviations of real gases from the Boyle-Mariotte law.

So for mercury near 0°, $k = \frac{dV}{V^2 dt} = 0{\cdot}000180$, at 100° = 0·000178, at 200° = 0·000175;† *i.e.*, the numerical value of k decreases with

* Such a dependence of the coefficient of expansion of gases from their molecular weight has been shown by me (*Compt. rend.*, February 14, 1876, and in my *Principles of Chemistry*, 4th edition, p. 156). As the coefficient of expansion of gases increases with increasing molecular weight, chlorine must have a large coefficient of expansion, and this should be taken into account in regard to the so-called dissociation of the chlorine molecule.

† It is known that the expansion of mercury determined from Regnault's experiments, shows many experimental inaccuracies, and this important point requires fresh investigation. If the expansion of mercury be calculated according to formula II, taking $k = 0{\cdot}0001775$, then at 100° V = 1·0181, instead of 1·0182, which number follows from the experiments, and for 300° V = 1·0562, instead of 1·0559. I think, therefore, that by applying the method of hydrostatic weighing of platinum with a known coefficient of expansion, determined according to Fizeau's method, more exact data for the real expansion of mercury may be obtained than by using the method of two corresponding tubes, or of two barometers. A platinum areometer will, possibly, best answer the purpose.

increasing temperature. The same would be the case with arsenic trifluoride, according to Thorpe's researches upon that rare substance. If k decreases, the difference of specific gravities $\frac{dD}{dt}$ will evidently decrease as regards its absolute value. The specific gravity of mercury is in reality at 0° = 13·596, at 100° = 13·353, at 200° = 13·113, at 300° = 12·878, and this gives kD_0 at 50° = 0·00243, at 150° = 0·00240, at 250° = 0·00235. The reverse kind of deviation (positive), namely, the increase of k with increasing temperature, is exhibited by the majority of other liquids, especially by liquid hydrocarbons rich in hydrogen and liquids of low boiling point and large coefficient k. As an instance I take the mean of Kopp's and Pierre's data for ether.

t =	0°	10°	20°	30°
V =	1·0000	1·0155	1·0317	1·0489
D =	0·7362	0·7250	0·7136	0·7019
$\frac{dD}{dt}$ * =	−0·00111	−0·00113	−0·00115	−0·00118
k =	0·00150	0·00153	0·00156	0·00159
$V=(1-0{\cdot}00154t)^{-1}$ =	1·0000	1·0156	1·0318	1·0485

The last line, calculated on the assumption of the ideal state, *i.e.*, with a constant value of k = 0·00154, shows that the difference between calculation and experiment is small also in this case; for the experiments of Kopp differ much more widely from those of Pierre. Thus at 10° (reduced to the air thermometer) the volume is 1·0153 according to Kopp, and 1·0156 according to Pierre.

As another instance I take diisobutyl, C_8H_{18}. Thorpe's experiments give—

t =	0°	20°	40°	60°	80°	100°
V =	1·0000	1·0243	1·0498	1·0771	1·1070	1·1401

Here the value of k increases rapidly with increasing temperature, as is apparent from the mean value of k from 0° to t°, viz.:—

$$k = \frac{V-1}{t.V_2} = 0{\cdot}001186 \quad 0{\cdot}001186 \quad 0{\cdot}001193 \quad 0{\cdot}001208 \quad 0{\cdot}001229 .$$

If in this case, in which the deviations are greater than in the majority of cases, the expression II is applied, we obtain—

$$V = (1-0{\cdot}0012t)^{-1} = 1{\cdot}0246 \quad 1{\cdot}0504 \quad 1{\cdot}0776 \quad 1{\cdot}1062 \quad 1{\cdot}1364$$

From this it is seen that here, especially near the boiling tempera-

* Limit of ratio between the rates of increase of D and of t.

ture, the deviations exceed the possible experimental errors,* which proves undoubtedly that small positive deviations from II exist, just as the expansion of real gases shows unmistakeable deviations from the expression $V = 1 + kt$.

As experiments prove the existence of some deviations from the ideal expansion on both sides, it is apparent that all other values for n, except $n = -1$ in the general formula $V = \left(1 + \frac{kt}{n}\right)^n$, will be less in accordance with reality and with the uniformity in the expansion of liquids than the first proposed approximation :—

$$V = \frac{1}{1-kt}.$$

The preceding results may be summed up as follows:—In the

* The determination of the absolute expansion of liquids involves, besides apparent and accidental experimental errors, especially the following ones : (1) the variation of the coefficient of expansion of the vessel with varying temperature is not taken into account (as seen distinctly from the experiments of Regnault, Recknagel, and others) ; (2) the determinations are, as a rule, carried on in uncovered long thermometer-like apparatus, and by this not only the possibility of diminution and change of part of the liquid occurs (this could still be taken into account), but a large column of the liquid reaches above the level of the bath, the correction for the temperature of which is very doubtful ; even the low temperature of the upper parts of the vessel gives rise to currents within the liquid, and this does not permit to assume a definite volume at the conditions of full equilibrium of temperature ; (3) no correction is made for pressure, and yet all liquids are compressible, and the pressure is different according to the different height of the column in the dilatometer and different stand of the barometer (all data should refer either to normal pressure or to pressure = 0) ; for this reason all data (especially for compressed gases which yield strongly compressible liquids) obtained in sealed tubes, in which the pressure varies greatly, prove not to correspond to reality ; (4) according to a generally accepted custom all investigators take the mean of experiments, in order to derive from it the probable absolute expansion, though they may apparently involve single occasionally erroneous determinations. Even among the data of such an excellent investigator as Thorpe, one is taken into the calculation, namely, that of arsenic fluoride (*loc. cit.*, p. 352) for 12·5°, though it apparently involves an occasional error ; (5) the indications of the mercurial thermometer are only rarely (Regnault, Thorpe) reduced to air thermometer ; (6) little trouble is taken in order to keep away moisture, but its presence will lessen the expansion of the majority of the liquids, &c.

P. de Heen (*Bulletin de l'Acad. Royale des Sciences Bruxelles*, 1882, p. 528) assumes, on the basis of different hypotheses, another law of dilatation, namely, $V\left(\frac{1}{1-1{\cdot}333\ \ldots\ .at}\right)^{\frac{3}{4}}$, and explains all deviations from this law only by dissociation in the physical or in the chemical sense. But as the deviations for mercury from De Heen's formula are very appreciable, and tend to another side (the expansion is smaller than it should be according to the formula) than that required by dissociation, and as the majority of liquids of high boiling temperature exhibit a smaller expansion than that which is required by De Heen's formula, it cannot be regarded at all as an expression of reality.

expansion of liquids a peculiar regularity and a qualitative uniformity is observed, and the first approximation to reality is expressed by the equation:—

$$V = (1-kt)^{-1}, \text{ or } D = D_0(1-kt),$$

in which k is a constant coefficient, which characterises each separate liquid, like the specific gravity, boiling point, capillary constant (a^2), and other fundamental data of that kind. Now as isomeric bodies often show remarkable differences in the value of this coefficient k, as it changes in general with the composition of the body, as the compressibility depends upon pressure, and, as the cohesion, specific gravity, and boiling point (the most volatile bodies have a large k, the liquefied gases an especially large one), as well as molecular weight, appear to be connected with the value of this coefficient, so an investigation, directed to the determination of its value and its change under different conditions (with change of temperature, pressure, composition, and electrical state) promises to become very important for the mechanics of liquids, as it may be expected to clear up the complicated dependence of volume upon temperature, find a true general law of expansion of liquids, and throw light upon the apparent deviations from the first approximation shown above. This, however, is by itself sufficient in the majority of physico-chemical investigations of liquid bodies, just as Gay-Lussac's law, though not absolutely exact, is sufficient in the majority of physico-chemical work with gases.

This coefficient k may be called the *determinator* of expansion. If the densities D and D_1 at the temperatures t and t_1 are known, then $k = \frac{D - D_1}{Dt_1 - D_1 t}$. If experiment yields volumes V and V_1 at t and t_1, then $k = \frac{V_1 - V}{t_1 V_1 - tV}$.

XX.—*On a Relation between the Critical Temperatures of Bodies and their Thermal Expansions as Liquids.*

By T. E. Thorpe, Ph.D., F.R.S., and A. W. Rücker, M.A.

Attempts have been made by various writers to bring the complicated phenomena of liquid expansion under some one comprehensive law.

In recent times Van der Waals has investigated a general relation between the pressure, volume, and temperature of bodies, which from

the agreement between experiment and the theoretical conclusions to which it points seems to be a close approximation to the truth (*see* "Die Continuität des Gasförmigen und Flüssigen Zustandes," by Prof. Van der Waals. Translated into German by Dr. F. Roth, Leipzig, 1881). This theory leads to the result that the thermal properties of bodies are comparable, when their absolute temperatures are the same fraction of their absolute critical temperatures, their pressures the same fraction of their critical pressures, and their volumes the same fraction of their critical volumes. Temperatures, pressures, and volumes, which in the case of any two bodies are the same fractions of those which characterise their critical points are said to correspond; and it is only when comparison is made under corresponding circumstances that the unity which underlies the apparent diversity in the thermal properties of bodies can be recognised.

Thus the want of similarity between the formulæ which express the expansions of liquids is due to the fact that their initial point is in general the arbitrarily selected temperature of melting ice, and that the same thermometric scale is employed for all alike. Uniformity of mathematical expression can be obtained only if in each case the temperature is expressed, not in ordinary thermometric degrees, but as a fraction of the absolute boiling point of the substance. If the bodies are compressible, the pressures to which they are subjected must also correspond.

By means of this theory it is possible to obtain the law of the thermal expansion of any one liquid from that of any other, provided their critical temperatures are known. Van der Waals thus calculates the formula for the expansion of ether from those of several other liquids. The results of observation and theory are in striking agreement, but the calculations are long and troublesome (*loc. cit.*, 154—155).

In a paper recently read before the Chemical Society Prof. Mendelejeff has given an extremely simple and accurate empirical formula for the expansion of liquids under constant pressure between 0° and their boiling points. The formula is—

$$(1.) \qquad 1/V_t = 1 - kt,$$

where V_t is the volume at $t°$ (that at 0° being unity) and k is a quantity which differs for different substances, but which may for any one substance be considered invariable between 0° C. and the neighbourhood of the boiling point.

Prof. Mendelejeff has tested this formula in the case of 47 liquids, the expansions of which have been determined by one of us (*Chem. Soc. J.*, March, 1880), and he finds a close agreement between the observed and calculated results.

As soon as we became acquainted with this fact, it occurred to us that Van der Waals' theory would probably throw some light on the relation between the values of k obtained for different substances; and in the present paper we propose to lay some of the results of our inquiries on this point before the Society.

One of the conclusions at which Van der Waals arrives is that the product of the coefficient of expansion under constant pressure into the absolute critical temperature is at corresponding temperatures the same for all bodies.

This may be expressed by putting—

$$(2.) \qquad \frac{1}{V_t}\frac{dV_t}{dt} \times T_1 = C$$

where T_1 is the critical temperature and C is a function of the temperature, but is independent of the material, provided the above condition be fulfilled.

Substituting in (2) from (1) we obtain—

$$(3.) \qquad T_1 k/(1 - kt) = C \text{ or } 1/k = T_1/C + t.$$

If now we assume

$$1/C = a - T/T_1,$$

where $T = 273 + t$, and a is a constant for all temperatures and substances, the conditions which C and k must fulfil are satisfied. For C is the same for all substances if they are compared at temperatures for which the fraction T/T_1 is the same, while the value of k, which is given by $1/k = aT_1 - 273$, is the same for all temperatures, but is different for substances with different critical points.

Substituting this value of k in equation (1), and putting the volume at 0° C. equal to V_0, we transform Mendelejeff's formula into—

$$(4.) \qquad \frac{V_0}{V_t} = \frac{aT_1 - 273 - t}{aT_1 - 273} = \frac{aT_1 - T}{aT_1 - 273}.$$

Hence since the densities are inversely proportional to the volumes—

$$(5.) \qquad \frac{D_t}{aT_1 - T} = \frac{D_0}{aT_1 - 273}.$$

This formula may be expressed in words as follows:—

The density of a liquid is proportional to the number obtained by subtracting its absolute temperature from its absolute critical temperature multiplied by a constant which is the same for all substances.

To test this law and determine the value of the constant a, those liquids only are available of which the laws of expansion and critical temperatures are known, and which satisfy the further condition that

the expansions can be approximately expressed by Mendelejeff's formula.

The chief uncertainty in the value of a for any given liquid arises from errors in the determination of the critical temperature. That the same observer, using throughout the same method of experiment, can obtain concordant results, is evident from the observations of Pawlewski, discussed at greater length below. He enunciates the law that there is a constant difference between the critical temperatures and boiling points of homologous compounds, and supports it by a number of examples in which the agreement between the differences in question is so close as to prove that the critical temperatures must be accurate to within a degree or two. The results of different observers display much greater discrepancies. Thus Pawlewski and Sajotschewsky find for the absolute critical temperature of methyl acetate, 512·8° and 502·8°, for that of ethyl acetate, 529·5° and 512·8° respectively. Sajotschewsky finds for ether, 463°, and for benzene, 553·6°, and the corresponding values obtained by Ramsay are 468·5° and 564·7°. These facts have led us to compare substances the critical temperatures of which were determined by the same observer.

If $V_0 = 1$ equation (4) may be written—

$$(6.) \qquad a = \frac{TV_t - 273}{T_1(V_t - 1)}.$$

By this formula the values of a given in the following tables have been computed. The letters P, K, and T attached to the values of V_t indicate that the expansions used in the calculations were determined by Pierre, Kopp, and Thorpe respectively.

In Table I we have grouped together a number of substances, the critical temperatures of which were determined by Sajotschewsky (Wiedemann, *Beiblätter*, 1879, 741).

TABLE I.

Substance.	t.	V_t.	T_1.	a.
Ethyl chloride	10	1·0160 P	455·6	1·993
Ether	30	1·0483 K	463·0	1·996
Benzene	80	1·1064 K	553·6	1·996
Ethyl formate	50	1·0735 K	503·0	1·995
Ethyl acetate	70	1·1040 K	512·8	1·981
Methyl acetate	50	1·0733 K	502·8	1·999
Chloroform	60	1·08179 T	533·0	2·001
			Mean ..	1·995

The agreement between the values of a in this table is very remarkable, considering the difficulty of the experiments from which its value is obtained.

The critical temperatures of ether and benzene determined by Ramsay (*Proc. Roy. Soc.*, **31**, 194—206) give different values of a. We have included them in the next table together with those of acetone and diethylamine, the critical points of which, as determined by Sajotschewsky, lead to very similar values of a, and with carbon bisulphide, which appears abnormal in so far that a is $= 2{\cdot}070$. The expansion of diethylamine was determined by Oudemans (Wiedemann, *Beiblätter*, 1883, 567).

TABLE II.

Substance.	t.	V_t.	T_1.	a.
Ether	30	1·0483K	468·5 R	1·952
Benzene	80	1·1064K	564·7 R	1 957
Acetone	50	1·07517T	505·8 S	1·953
Diethylamine	50	1·0787O	593·0 S	1·947
Carbon bisulphide	40	1·0489T	544·8 S	2·070
			Mean ..	1·976

We have calculated the values of a for many of the bodies from their expansions between 0° and 10°. These, as was to be expected from the short range of temperature, are more variable, and are on the whole larger than those given above. This is in accordance with the fact that Mendelejeff's constant k varies slightly with the temperature.

We have also tried whether closer agreement could be obtained by comparing the substances at corresponding temperatures. The comparison in this case was under conditions less favourable for the application of Mendelejeff's formula, and the results are not so good. On the whole therefore the best plan seems to be to take the whole range over which his formula extends, *i.e.*, from 0° to the boiling point or to a temperature a little below it.

It is, however, of little use attempting refinements of any kind till determinations of critical points by different observers are in closer agreement. The discrepancies may perhaps, as Van der Waals suggests, be due to the influence of impurities, the effects of which are inappreciable at lower temperatures. However this may be, Tables I and II indicate that the values of a obtained for different substances differ but little more than do those calculated for the same substance from data supplied by different observers.

In the case of the three substances included in the second table and not included in the first, viz., carbon bisulphide, acetone, and diethylamine, probabilities of error can be pointed out which do not exist in the case of those mentioned in Table I.

Thus the critical point of carbon bisulphide may be affected by the alterations which exposure to light is known to produce in it (*cf.* Herwig, *Pogg. Ann.*, **137**, 19 and 592).

Sajotschewsky gives 232·8° C. as the critical temperature of acetone, but remarks in a note, that "after longer experiment the critical temperature rose to 237·5°." The critical temperature of this substance is thus very uncertain.

The expansion of diethylamine has been determined by Oudemans, but there seems to have been some question as to the purity of the material, and though Van der Waals uses the formula to find the density at 18°, the error (if any) at so low a temperature might be less than at 50°. The formula for the expansion was obtained from observations at four temperatures only, and is therefore probably less accurate than those from which our data have been obtained in other cases (*cf.* Van der Waals, *loc. cit.*, 163—164).

We have excluded alcohol from our comparisons, as different observers find critical points for this substance which differ by 22°.

The investigations of Pawlewski (*Ber.*, **15**, 2460—2464, 1882; *Ber.*, **16**, 2633—2636) afford the greatest number of determinations of critical points which can be used for calculating the value of a. In the case of many of the substances the expansion has been determined only between 0° and the boiling point. We have therefore taken t as the boiling point itself, instead of a temperature a little below it. We have omitted bodies for which the lower temperatures differed from 0°, as the number of examples for which the requisite data exist in the most convenient form were sufficient for our purpose.

The agreement between the values of a in Table III is much less close than in Table I. The mean value is however nearly the same in each case.

The expansion of allyl chloride and propionic acid was determined by Zander (*Liebig's Annalen*, **214**, 138).

The critical temperatures of allyl chloride and of ethylene chloride are marked by Pawlewski as less accurately determined than the others.

TABLE III.

Substance.	t.	V_t.	T_1.	a.
Allyl chloride	46·0	1·0675 Z	513·7	1·95
Ethyl bromide	40·0	1·0578 P	509·0	1·98
Propionic acid	140·5	1·1781 Z	612·9	1·96
Diisobutyl	108·5	1·1553 T	543·8	1·99
Phosphorus trichloride	75·9	1·0983 T	558·5	2·01
Carbon tetrachloride	81·3	—	507·9	1·96
Ethylene chloride	83·5	1·1076 T	556·0	2·04
Ethydene chloride	59·9	1·0854 T	527·5	1·96
Acetic acid	118·5	—	594·5	2·04
Toluene	109·2	—	593·8	2·02
			Mean ..	1·991

In the next table we have placed together a number of isomeric and homologous ethers, the critical temperatures of which were determined by Pawlewski and the expansions by Elsässer (*Liebig's Annalen*, **218**, 302). The values of a agree about as well as in the last table, but the mean value is much less.

TABLE IV.

Substance.	t.	V_t.	T_1.	a.
Propyl formate	81·0	1·1180	540·4	1·93
Isoamyl „	123·3	1·1611	577·6	2·01
Methyl acetate	57·1	1·0873	512·8	1·92
Ethyl „	77·1	1·1175	529·5	1·90
Propyl „	100·8	1·1444	555·4	1·93
Isobutyl „	116·3	1·1574	568·8	1·98
Methyl propionate	79·9	1·1197	535·7	1·90
Ethyl „	98·3	1·1424	553·6	1·93
Propyl „	122·2	1·1683	577·8	1·94
Isobutyl „	136·8	1·1926	591·7	1·89
Ethyl butyrate	119·9	1·1692	577·3	1·91
Propyl „	142·7	1·1975	599·6	1·90
			Mean ..	1·93

On the whole then, these calculations point to the conclusion that a is within narrow limits a constant, and that the larger discrepancies in the results deduced from Sajotschewsky's observations occur in the

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case of substances the properties of which are known to be determined with the least accuracy. Pending further investigation, therefore, we think we are justified in assuming that there is a large class of liquids for which a is to within the limits of the error of experiment constant, and very nearly $= 2$.

If we insert this value in equations (4) and (5), they assume the extremely simple forms—

$$\frac{V_0}{V_t} = \frac{2T_1 - T}{2T_1 - 273} \text{ or } \frac{D_t}{2T_1 - T} = \frac{D_0}{2T_1 - 273}.$$

The latter of these equations leads to the law that *the density of a liquid is very nearly proportional to the number obtained by subtracting its absolute temperature from twice its absolute critical temperature.*

Prof. Mendelejeff suggests that just as the expansion of a perfect gas is expressed by the formula $V_t = V_0(1 + \alpha t)$, so that of a perfect liquid is given by $V_t = V_0/(1-kt)$. If we may apply this speculation to our own results, it may be expressed by saying that the formulæ

$$\frac{V_t}{V_0} = \frac{T}{273} \text{ and } \frac{V_t}{V_0} = \frac{2T_1 - 273}{2T_1 - T}$$

express very approximately the expansions under constant pressure of a perfect gas and a perfect liquid respectively.

In the case of real liquids, the mean value of a (deduced from Table I) seems to be more nearly 1·995, and we now propose to give a couple of examples showing the accuracy and ease with which the volume of a liquid included in this table can be calculated when this value is used.

Selecting benzene as a substance, the expansion of which has been often determined, we have—

$$1{\cdot}995\ T_1 - 273 = 831{\cdot}43.$$

Hence the volume at 20° $= 831{\cdot}43 \div 811{\cdot}43 = 1{\cdot}0246$, and so on.

Table V contains in four parallel columns the relative volumes of benzene at different temperatures, as determined by Kopp (*Jahrb. f. Chem.*, 1847–8, 65), Longuinine (*Jahrb. f. Chem.*, 1867, 48); Pisati and Paternò (*Chem. Soc. J.*, 1874, 686); and Adrieenz (*Ber.*, **6**, 442). In the last column are the values given by the formula.

TABLE V.—*Expansion of Benzene.*

t.	Kopp.	Louguinine.	Pisati and Paternò.	Adrieenz.	Calculated.
0	1·0000	1·0000	1·0000	1·0000	1·0000
15	1·0180	..	1·0180	1·0176	1·0184
20	1·0241	1·0240	..	1·0237	1·0246
25	1·0303	..	1·0308	1·0298	1·0310
40	1·0496	1·0498	..	1·0489	1·0505
50	1·0630	..	1·0606 (?)	1·0623	1·0640
60	1·0769	1·0774	..	1·0764	1·0778
75	1·0988	..	1·0986	1·0990	1·0991
80	1·1064	1·1069	..	1·1070	1·1064

The value of a found for ethyl acetate differs considerably from 1·995. The difference between the observed and calculated results is nevertheless little more than the error of experiment.

TABLE VI.—*Ethyl Acetate.*

t.	Kopp.	Calculated.
0	1·0000	1·0000
10	1·0130	1·0135
30	1·0405	1·0417
50	1·0706	1·0714
70	1·1040	1·1029

It is not, however, so much as affording a ready means of calculating the volume of a liquid at a given temperature, as by supplying a method of deducing the critical temperature from the expansion at comparatively low temperatures, that the formula will be useful, if the limits of the variation of a are found to be sufficiently small.

To illustrate this we calculate the critical temperatures of the substances in Table I, assuming $a = 1{\cdot}995$ (its mean value deduced from that table), and using the formula—

$$T_1 = \frac{TV_t - 273}{1{\cdot}995(V_t - 1)}.$$

The error is in all cases seen to be much less than the differences between the results of different observers.

TABLE VII.—*Critical Temperatures.*

	Observed.	Calculated.	Difference.
Ethyl chloride	455·6	455·2	−0·4
Ether	463·0	463·8	0·3
Benzene	553·6	553·8	0·2
Ethyl formate	503·0	502·9	0·1
Ethyl acetate	512·8	509·3	−3·5
Methyl acetate	502·8	503·9	1·1
Chloroform	533·0	534·8	1·8

We may sum up the results of our inquiry as follows:—

(1.) Mendelejeff has proved that the expansion of a liquid can be expressed by a very simple formula containing only one constant, which is different for different liquids. We have shown, by applying Van der Waals' theory to this result, that the reciprocal of the constant is the number obtained by subtracting 273 from the product of the critical temperature into a quantity which should be the same for all substances.

(2.) The values of this quantity a obtained from different substances, for which the required experimental data exist, and to which Mendelejeff's formula applies, are found to be approximately constant. In the case of seven substances, the values of the critical temperatures determined by Sajotschewsky lead to the values of a, none of which differs by 0·8 per cent. from the mean. The value of a approaches very closely to 2.

(3.) If further investigation proves that the range of variations in the value of a is small, the formula given would afford a ready and valuable means of calculating the critical temperatures of bodies from observations on their expansions as liquids.

XXI.—*Note on* (I) *the Behaviour of the Nitrogen of Coal during Destructive Distillation, and* (II) *a Comparison of the Amounts of Nitrogen left in Cokes of Various Origin.*

By WATSON SMITH.

MR. WM. FOSTER at the close of his interesting paper read before this Society, and published in this Journal (1833, Trans., 105—110), summarises his results as follows:—

Percentage of nitrogen in the coal	1·730
Percentage of nitrogen of coal evolved as ammonia during destructive distillation	0·251
Percentage of nitrogen in coal evolved as cyanogen during destructive distillation	0·027
Amount of nitrogen remaining in coke furnished by 100 parts of coal	0·842
	1·120
Nitrogen from 100 parts of coal unaccounted for, the larger portion of which is presumably present as free nitrogen in the coal-gas. Some is no doubt in the tar	0·610

If we further reduce these figures to percentages on 100 parts of nitrogen, their relation to each other becomes more intelligible:—

Nitrogen of coal evolved as ammonia	14·50
Nitrogen of coal evolved as cyanogen	1·56
Nitrogen of coal present in the coal-gas in the elementary condition	35·26
Nitrogen of coal remaining behind in the coke	48·68
	100·00

"I have not made any experiments on the amount of nitrogen in the tar, nor am I in possession of any information on the subject, but I have assumed that the quantity is relatively small."

Mr. Foster's last remark referring to the amount of nitrogen in the tar interested me on first reading it, and for the following reason:—As far back as the year 1868, when making distillations either of coal-tar or crude coal-tar oils, I observed, whenever the distillations were carried so far that pitch remained in the retort, and these residues of pitch were further heated until partial coking took place, that on leaving the whole to cool partially, and then removing the stopper of the retort, a smell of ammonia was always perceptible, reddened litmus-paper was turned blue, and a stopper moistened with hydrochloric acid fumed strongly. I have also been informed more recently by tar distillers that after coking pitch, when the man-hole lids of the stills have been removed, the odour of ammonia is very powerful. The experiment is so easily performed with a little hard pitch broken up small and placed in a retort and heated to coking, that it would form a very good lecture experiment, to illustrate the fact that nitrogen compounds of considerable stability exist in hard pitch, and in partially coked pitch, and that at temperatures near the softening point of glass, these compounds are so decomposed, that on

partial cooling and in contact with moist air, ammonia is evolved. It is a remarkable fact that not the slightest smell of ammonia could be perceived, if the retort-stopper were removed whilst the retort is still very hot. The most favourable time for obtaining the evidence of the presence of ammonia is when the retort has cooled so far that its bulb may be held in the hand.

My supposition all along has been that the nitrogen in the partially coked pitch has been brought into so unstable a form of combination; and that, on cooling down and a back-suction of moist air into the retort taking place, such unstable nitrogen compounds in the highly porous mass in presence of moisture, are decomposed or altered so as to yield ammonia.

It was determined to attempt to estimate the amount of nitrogen in ordinary coal-tar and in the oils obtained at different stages from that tar, as well as in the pitch left as a residue. The numbers given are the means of at least two experiments for each sample.

The tar analysed was thoroughly well settled from ammoniacal water, but beyond this no attempt was made to remove suspended solution of ammoniacal salts.

The crude benzene contained ammonia in solution, which communicated to it a pungent odour. The "light oil" likewise smelt slightly of ammonia, but the "creosote oil" was quite free from ammoniacal odour.

Nitrogen in the Tar.—The mean of two experiments gave — 1·667 per cent.

Crude benzene, obtained from the above tar (mean of two experiments)	= 2·327
"*Light oil*," obtained from the above tar (mean of two experiments)	= 2·186
"*Creosote oil*," obtained from the above tar (mean of two experiments)	= 2·005
Red oil, or Oils from which the crude anthracene has been separated by filtration (mean of two experiments)	= 2·194
Pitch, obtained from the above tar (mean of two experiments).....	= 1·595

It would thus appear that nitrogen compounds of high boiling points occur in the oils drained from the crude anthracene to a considerable extent, and that though there is a falling off in the pitch (in the above case a hard pitch), yet still in this product certain very stable nitrogen compounds occur; further, that the amount of nitrogen contained in ordinary coal-tar oils (from Lancashire coal-tars) may be stated as 2 per cent. on the average.

Of course the lighter naphthas will contain the pyridine bases, the intermediate naphthas and oils, more especially the quinoline bases, whilst the anthracene oils and pitch will contain the carbazols and acridine, and possibly other nitrogenous bodies of high boiling and melting points not yet examined.

II. *Comparison of the Amounts of Nitrogen left in Cokes of Various Origin.*—Three varieties of coke were now analysed, with the object of determining the nitrogen in them, viz.:—

(1.) Ordinary gas-retort coke.

(2.) Beehive metallurgical coke.

(3.) The hard compact metallurgical coke from the Simon-Carvès coke-ovens.

The results are as follows:—

Kind of coke examined.	Percentage of nitrogen found.
(*a*.) Ordinary gas-retort (mean of two experiments)	1·375
(*b*.) Beehive metallurgical coke (mean of two experiments)	0·511
(*c*.) Metallurgical coke from the Simon-Carvès coke-ovens (mean of three experiments)....	0·384

From the above results it may, I think, be concluded that in (*a*) the effect of a sharp heat of short duration is shown under the usual circumstances of gas-retort work, not to be so efficacious in decomposing certain very stable nitrogen compounds so as to drive the nitrogen out of the coke, as a long-continued high temperature such as is found in (*c*). In (*a*) a charge of from 2—3 cwts. of coal is heated for 6 hours, whereas in (*c*) a charge of 4 tons is heated for about 40 hours. The temperatures employed are not much unlike in (*a*) and (*c*), though on the whole the heat of the Simon-Carvès oven will be the stronger.

No note was taken or inquiry made as to the *part* of the interior of the ovens from which the cokes under examination were taken. In the case of gas-retort and Simon-Carvès oven cokes no such note or inquiry is necessary, since in both cases external heat is uniformly applied to the mass of fuel disposed in a thin layer, which in the former case is arranged horizontally, in the latter vertically. With the Beehive coke, certain differences of temperature might occur in different parts of the mass; *e.g.*, the portions of coke lying nearer the surface of the mass in the ordinary Beehive, and nearer the small air-inlet, but not necessarily nearer the walls (not externally heated, but rather cooled) might be expected to have been more strongly heated than those lying next the floor of the oven. In the Jameson oven the temperature throughout the coking and coked mass will be much more

uniform than in the ordinary Beehive. In the above-mentioned experiments, simply a well-burnt sample of Beehive coke was taken for examination, exhibiting an average appearance and texture.

The analyses recorded in this note were made by Mr. R. J. Gow in the Chemical Laboratory of the Owens College, and to him I beg to express my best thanks.

The apparatus used for collecting and measuring the nitrogen was that of Staedel, which possesses the considerable advantage over the usual apparatus, that the hands of the operator are spared, there being no necessity to bring them into contact with the caustic alkaline solution.

For the removal of air from the materials and interior of the combustion tube, a Swan's modification of the water air-pump was used, the washing action of the carbonic acid from the heated magnesite being aided by the exhaustion.

XXII.—*Studies on Sulphonic Acids.* No. I. *On the Hydrolysis of Sulphonic Acids and on the Recovery of the Benzenes from their Sulphonic Acids.*

By Henry E. Armstrong, F.R.S., and A. K. Miller, Ph.D.

It has long been known that several of the benzenes—using this term to indicate benzene and its true homologues—may be recovered from their sulphonic acids by dry distillation (Freund, *Annalen*, **120**, 80; Beilstein, *ibid.*, **133**, 36), but the reaction is necessarily by no means of a simple character, and consequently the yield of hydrocarbon is unsatisfactory.*

A method of hydrolysing sulphonic acids which permits of the complete recovery of the parent-compound was (we believe for the first time) employed by one of us in conjunction with C. L. Field, in the course of an examination of coal-tar cresol, and consisted in heating the sulphonate with muriatic acid under pressure (*Chem. News*, 1874, **29**, 282; *Ber.*, 1874, **7**, 406). This method has since been of signal service in the hands of various chemists, but there is the practical objection to its use, except on the small scale, that the decomposition has to be effected in closed vessels; and as the temperature at which

* H. Caro recommends that, instead of the sulphonic acid, its ammonium salt be distilled, and according to V. Meyer (*Ber.*, 1882, **16**, 1468), in the case of thiophene, a much better result is thus obtained.

it takes place is in many cases somewhat high, loss from explosion of the tubes is not unfrequently incurred.

Although it would appear to be obvious that sulphuric might be substituted for muriatic acid to promote hydrolysis, we are acquainted with only one instance of its employment: to recover metaxylene from its sulphonic acid, Jacobsen (*Ber.*, 1878, **11**, 19) recommends distillation of a mixture of 10 parts sodium metaxylenesulphonate, 5 parts sulphuric acid and 1 part water; but we are under the impression that the same chemist has somewhere stated that he had prepared cymene by distilling its sulphonic acid with sulphuric acid.

We were led to investigate the behaviour of sulphonic acids on distillation with sulphuric acid in the course of our study of the hydrocarbons resulting from the action of dehydrating agents upon camphor, our primary object having been to find a method of separating the 1:2:3:5 tetramethylbenzene from admixed hydrocarbons. One of us in 1878 (*Chem. News*, **38**, 5; *Ber.*, **11**, 1697) had devised a process for separating mesitylene and pseudocumene by heating the mixture of their sulphonic acids with muriatic acid at 100°, whereby the mesitylenesulphonic acid alone is hydrolysed, the pseudocumene being afterwards recovered by heating at 130—140°; and it had long been known to him that if mesitylene be dissolved in sulphuric acid, it may readily be recovered by merely passing steam into the solution. It therefore appeared probable that the tetramethylbenzene which is formed on methylating mesitylene would likewise form a highly unstable sulphonic acid. It was found, however, on passing steam into the solution in sulphuric acid of the mixture of hydrocarbons from camphor, that not merely the tetramethylbenzene but all the benzenes could without difficulty be recovered. The knowledge thus gained has nevertheless proved of the greatest service, as it has enabled us, dealing with large quantities, to separate the benzenes from hydrocarbons of other series, and to easily recover benzenes from pure sulphonates.

Our method consists in merely passing steam through the solution of sulphonic acid or sulphonate in sulphuric acid, the acid solution being heated and maintained at the temperature at which hydrolysis takes place with fair rapidity. In commencing the operation, if no hydrocarbon distils over, sufficient heat is applied to concentrate the solution more and more, and when the required degree of concentration is attained, *i.e.*, when the temperature of the liquid is sufficiently high, the flame is so regulated that steam passes through the solution without condensing. It is desirable, as a rule, to add a considerable amount of sulphuric acid, not because the rate of hydrolysis very materially depends upon the presence of a large excess of acid, but in order to retain a sufficient bulk of liquid in the retort or flask when operating at a high temperature. We have usually found it con-

venient to add a weight of acid about equal to that of the sulphonate taken; when so large an excess of acid is used, no difficulty arises from the separation of solid sulphate, even if barium, calcium, or lead sulphonates be submitted to distillation. Operating in this way, we have not found the slightest decomposition to occur in the case of any of the numerous benzenes whose behaviour we have studied; we have therefore no hesitation in advising the employment of the method in all cases in which benzenes occur mixed with other hydrocarbons from which it is desired to separate them in a state of purity, and also in all cases in which it is desired to recover benzenes from their sulpho-compounds. Two practical illustrations of the value of the method have already been given by ourselves (*Ber.*, 1883, **16**, 2255, 2748*). The yield of hydrocarbon may be said to be theoretical, loss being incurred only (*a*) through dissolution of a small quantity of hydrocarbon by the water; (*b*) through incomplete separation of hydrocarbon from the water; and (*c*) through evaporation of the hydrocarbon. Of these the last only may become serious in the case of the more volatile hydrocarbons, and should be specially guarded against.

The difference in stability of mesitylene- and pseudocumenesulphonic acids led us to anticipate that similar differences would be found to obtain between the sulphonic acids of other hydrocarbons, and we have therefore studied the behaviour of as many as possible. The pure sulphonic acid or sulphonate was introduced, together with a considerable excess of sulphuric acid, into a retort or distillation

* It is well known that it is impossible to obtain the higher homologues of toluene from coal-tar naphtha by fractional distillation, on account of the presence of hydrocarbons of other series. These are in part soluble, and in part insoluble, in sulphuric acid (Jacobsen, *Annalen*, **184**, 200; *Ber.*, **10**, 1009; Nölting, *ibid.*, **17**, 267). Oliveri has stated (*Gazzetta*, 1882, 158) that on warming xylene with sulphuric acid on the water-bath he obtained a hydrocarbon boiling at about 295°, to which he attributes the formula $C_{16}H_{18}$; he appears to regard it as dixylyl, $(C_8H_9)_2$, formed by the action of the acid upon xylene. We also have observed the production of this hydrocarbon from commercial xylene, but have never obtained it on treating xylene, recovered from its sulphonic acid, with sulphuric acid. The hydrocarbon in question is probably a polymeride of an unsaturated hydrocarbon present in commercial xylene.

Moreover, to purify xylene or pseudocumene, it is not sufficient to merely convert the commercial products into sulphonic acids and form salts of the latter. On hydrolysing crude sodium metaxylenesulphonate directly prepared from commercial xylene, we have always observed that a comparatively large amount of black carbonaceous matter remains in the retort, while pure sulphonate does not yield a trace. Crude pseudocumenesulphonate exhibits a similar behaviour. The presence of this "sulphonate" in the mixture obtained on heating commercial xylene with sulphuric acid most seriously affects the separation of orthoxylene from metaxylene in the manner proposed by Jacobsen.

flask provided with a thermometer and steam-tube dipping into the liquid; heat was applied, steam being continually passed through the solution, and the temperature noted at which hydrocarbon began to distil over.

The following results were thus obtained:—

Name of acid.	Temperature of initial hydrolysis.
Benzenesulphonic acid	about 175°
Toluneparasulphonic acid	„ 150
Metaxylenesulphonic acid Orthoxylenesulphonic acid Paraxylenesulphonic acid*	„ 120
Pseudocumenesulphonic acid	„ 115
Mesitylenesulphonic acid	„ 100
Cymenesulphonic acid	„ 130
1 : 2 : 3 : 5 Tetramethylbenzenesulphonic acid.. Metamethylisopropylbenzenesulphonic acid .... 1 : 2 : 4 Dimethylethylbenzenesulphonic acid ..	„ 120

These results justify the hope that it will be found possible to separate many hydrocarbons by "fractional hydrolysis" of mixtures of their sulphonic acids. There are, however, several practical difficulties in the way of effecting this always by mere distillation. Thus the rate at which change takes place at or near the temperature of initial hydrolysis is extremely slow. For example, on distilling a dilute solution of pseudocumenesulphonic acid containing but a small proportion of sulphuric acid, water and hydrocarbon came over at various temperatures in the proportions shown in the following table:—

* On consideration of the results here tabulated, it is obvious that the sulphonic acids which are most stable, are those which are least readily produced when ordinary sulphuric acid is used as sulphonating agent, the only apparent exception being paraxylenesulphonic acid. According to Jacobsen (*Ber.*, **10**, 1009) "Beim Schütteln des rohen Theerxylols mit gewöhnlicher Schwefelsäure werden selbst in der Wärme nur geringe Spuren von Paraxylol gelöst." This, however, is not the case, as paraxylene may be dissolved by well agitating it with ordinary acid almost as easily as pure metaxylene, and therefore it does not materially differ from all other known benzenes in the manner hitherto commonly supposed.

Temperature of liquid.	c.c. of hydrocarbon collected.	c.c. of water collected.
115°	Slight film on water	—
115—118	0·1	320
120—140	0·8	230
118—125	0·3	300
122—125	0·6	370
—	0·6	360
—	0·7	400
—	0·6	400
—	0·5	400
—	0·5	370
—	0·75	440
124—128	0·7	450

The same solution was distilled with a larger proportion of sulphuric acid with the following results:—

Temperature of liquid.	c.c. of hydrocarbon collected.	c.c. of water collected.
115°	0·05	400
115—118	0·2	320
118—124	0·7	370
122—123	1·1	350
123—127	1·4	400
130—140	1·9	400

A somewhat large quantity of metaxylenesulphonic acid distilled with acid behaved as follows:—

Temperature of liquid.	c.c. of hydrocarbon collected.	c.c. of water collected.	Percentage of hydrocarbon in distillate.
About 120°	2·5	1000	0·24
120—125	5·5	1020	0·53
125—128	11·0	1020	1·06
128—138	32·0	1000	3·1
138—142	32·0	550	5·5
142—150	35·0	600	5·5
145—155	61·0	1150	5·0
155—157	23·0	1150	2·0

On this account, and as the rate at which hydrolysis proceeds also depends upon the mass of sulphonic acid present, it becomes necessary to distil at a temperature considerably above that at which the sulphonic acid of the particular hydrocarbon which it is desired to isolate begins to undergo change, and it may be therefore that the temperature is so high that the sulphonic acids of other hydrocarbons

are also hydrolysed. For example, if a mixture of mesitylene- and pseudocumenesulphonic acids be distilled at a temperature not exceeding about 105°, the major portion of the mesitylene is recovered free from pseudocumene; but in order to obtain the remainder, the distillation must be carried on at 105—115°, and a good deal of pseudocumene then passes over. Just as in ordinary quantitative separations, however, a precipitate is often dissolved and reprecipitated in order to render a separation complete, so in our case the intermediate fraction may be dissolved in sulphuric acid and redistilled: it is then possible to effect an almost complete separation. By combining our method with that which Jacobsen has rendered such service by introducing, namely, crystallisation of the sulphonic acids from a sulphuric acid solution, complete purification of many hydrocarbons may be very readily effected.

Preliminary experiments have shown that the temperature at which hydrolysis takes place in sealed tubes is not always the same as that at which it occurs when the solution is distilled. Thus, the mesitylene was completely recovered on heating its sulphonic acid at about 110° (in toluene vapour), while pseudocumenesulphonic acid remained unaffected, but was decomposed at about 130°. Metaxylenesulphonic acid underwent hydrolysis at 138° (in xylene vapour), a temperature which, however, did not suffice to change ortho- and para-xylenesulphonic acids; these latter and toluene-parasulphonic acid were hydrolysed at about 160°. Similarly metacymene was found to be more easily recovered than paracymene. We therefore now propose to study with the greatest care the hydrolysis of a variety of sulphonic acids under pressure, taking into account all circumstances which influence the rate of change, such as the amount of free sulphuric acid, mass of sulphonic acid, temperature and time. The results cannot fail to be of value as a contribution to our knowledge of the behaviour of corresponding derivatives of isomeric and homologous bodies, and it is more than probable that it will be possible sooner or later to devise methods which may serve for the quantitative analysis of mixtures of benzenes and of other compounds which are convertible into sulphonic acid.

As yet we have examined but few sulphonic acids of compounds other than benzenes. Naphthalene-β-sulphonic acid begins to undergo hydrolysis at about 135°. Phenolparasulphonic acid at about 116° paracresolorthosulphonic acid apparently at a slightly higher temperature, viz., 120°; and parisobutylphenolorthosulphonic acid at; about 110°.

It is our intention to extend these experiments to other sulphonic acids, and we expect soon to be able to give some practical illustrations of the use of our method.

XXIII.—*Note on the Preparation of Marsh-Gas.*

By J. H. Gladstone, Ph.D., F.R.S., and Alfred Tribe, F.I.C., F.C.S., Lecturer on Chemistry at Dulwich College.

In 1873 (*Chem. Soc. J.*, **26**, 682) we described two reactions in which marsh-gas was produced free from other hydrocarbons. The reactions were brought about by the action of the copper-zinc couple on methyl iodide in presence of water or alcohol, in accordance with the equations—

$$(a.)\ CH_3I + H_2O + Zn(Cu) = CH_4 + Zn\begin{matrix}I\\HO\end{matrix} + (Cu).$$

$$(b.)\ CH_3I + C_2H_6O + Zn(Cu) = CH_4 + Zn<\begin{matrix}I\\C_2H_5O\end{matrix} + (Cu).$$

The experiments which enabled us to deduce these equations were made on a somewhat small scale, and no attempt was made to prevent the methyl iodide from being carried away by the gas. The loss from this cause was in fact considerable. In presence of water, for example, 23 per cent. of the organic iodide was lost in this way; and, in presence of alcohol, when the action was allowed to proceed by itself, there was a loss of 52 per cent., and even when the containing vessel was kept immersed in cold water, the loss amounted to 43 per cent.

It was evident, however, that the reaction in which alcohol took a part, supplied the basis of a simple and expeditious method for preparing marsh-gas in a state of purity. We have now the pleasure of communicating to the Chemical Society an account of the modifications in our original experiments, which place the preparation of marsh-gas among the most simple of chemical operations. We employed in the old experiments the expensive zinc-foil, but we find that this may be replaced by the metal in the ordinary granulated condition.

Experiment I.—550 grams of somewhat thinly granulated zinc were placed in a flask *a* (see figure) having a capacity of 600 c.c., and 150 grams in a glass tube *b*, 12 inches long by 1 inch internal diameter, which is intended to serve the double purpose of a copper-zinc couple scrubber, and an inverted condenser. To prevent any finely divided copper or zinc from dropping from *b* to *a*, the orifice of the tube which connected the two parts of the apparatus was covered with copper gauze. In order to prepare the couple, the zinc was treated for a few minutes with dilute sulphuric acid, and washed twice or three times

with water. A 2 per cent. solution of copper sulphate was poured on to the clean metal and allowed to remain until nearly or completely decolorised. The solution of $ZnSO_4$ was poured off, and the treatment with the dilute copper solution, &c., repeated three times. The couple was washed three or four times with water until the sulphate was practically removed. The water was next replaced by ordinary rectified alcohol, sp. gr. 0·805, which, after a few minutes, was poured away; the vessels were filled again with alcohol, and again after a little while this was poured off, leaving the now prepared couple wet with alcohol.

The parts of the apparatus being put together, 20 c.c. (45 grms.) of methyl iodide were poured into the tap funnel *c*, together with an equal volume of alcohol, and the mixture allowed to run into *a*. The reaction expressed by equation (*b*) commenced at once, and the gas was collected over water (temp. 30° C., barom. 749 mm.). The 1st litre of marsh-gas was evolved in 8 minutes; the second in 11 minutes; the 3rd in 12 minutes; the 4th and 5th each in 11 minutes; the 6th in 15 minutes; the 7th in 27 minutes. We now ceased observing, but during the night 500 c.c. more of the gas were collected, making a total of 7500 c.c., which corrected for temperature, pressure, &c., correspond to 7053 c.c. As the theoretical amount of marsh-gas capable of being produced from 45 grams of the iodine is only 7100, this shows that the loss is almost entirely prevented by this modification of the process, 99·3 per cent. of the possible amount of marsh-gas having been obtained.

Experiment II.—In this experiment 650 grams zinc were placed in the flask, the difference in weight being due to the greater thickness of the granulated metal. In all other respects the preliminaries of this experiment were similar to Experiment I. As before, marsh-gas was immediately evolved on pouring the mixture of methyl iodide and alcohol (20 c.c. of each) into the flask. The 1st litre was collected in 9 minutes; the 2nd in 10; the 3rd in 15; the 4th in 16; the 5th in 20; the 6th in 30; and the 7th in 96 minutes. 40 c.c. of the iodide mixed with 20 c.c. of alcohol were now introduced into the flask, by the funnel *c*, and 20 c.c. more alcohol were added little by little, and from time to time, during the evolution of the gas, by the funnel *d*. The 8th litre of marsh-gas was collected in 11 minutes; the 9th in 23; the 10th in 31; and the 11th in 45 minutes. The bottom of the flask was next immersed about 2 inches in water at 40°, and the water

kept at this temperature. The 12th litre of gas was collected in 22 minutes; the 13th in 10 minutes; the 14th, 15th, 16th, and 17th each in 11 minutes; the 18th in 13; and the 19th in 20 minutes. We now ceased collecting the gas, but in about 12 hours the action was found to be completed. This shows that the process can be greatly expedited, if desired, by raising the temperature.

The gas, as it left the delivery tube, contained traces of methyl iodide and alcohol, from which of course it may be separated by well known methods.

XXIV.—*On the Action of Dibrom-α-Naphthol upon Amines.*

By Raphael Meldola.

In a preliminary note published at the beginning of last year (*Chem. News*, Jan. 19th, 1883), I called attention to the remarkable facility with which dibrom-α-naphthol entered into reaction with certain amines,* forming in the case of aniline, paratoluidine, and β-naphthylamine, well characterised crystalline bases. The action of this dibromnaphthol upon diamines has been made the subject of a patent by the firm of L. Casella and Co. (Germ. Pat., No. 20,850, May 31st, 1882), who have shown that this reaction gives rise to the colouring matters of the "indophenol" class mixed with a certain percentage of the "naphthol violet" colouring matters discovered by the author of the present paper (*Chem. Soc. J.*, 1881, Trans., p. 37). This reaction has been recently investigated by R. Möhlau (*Ber.*, 1883, p. 2843), and in the present paper I will therefore confine myself to the results of the action of dibrom-α-naphthol upon monamines, the experiments described herein having been commenced more than two years ago in Messrs. Brooke, Simpson, and Spiller's laboratory at the Atlas Works, Hackney Wick.

Action upon Aniline.

On mixing dibrom-α-naphthol with about three times its weight of

* The production of a splendid blue colouring matter (most probably a triphenylrosaniline) can be shown as a lecture experiment by heating diphenylamine and dibrom-α-naphthol for a few minutes in a test-tube. The contents of the tube when cool can be boiled out with alcohol and poured into a beaker of alcohol in order to show the colour to advantage.

aniline, the mixture, if allowed to stand in the cold, soon solidifies to a white crystalline mass of aniline dibromnaphtholate,

$$C_6H_7N,C_{10}H_5Br_2HO.$$

On raising the temperature to near the boiling point of aniline, the contents of the flask gradually acquire a deep reddish-brown colour, and crystals begin to separate. The reaction is complete in about ten minutes, and when once commenced proceeds spontaneously, so that it is better to remove the flask from the source of heat. When cool, the mass forms a solid cake of crystals. The latter are washed with cold alcohol to remove excess of aniline and then purified by several crystallisations from boiling alcohol. The substance thus formed orange-red needles melting at 179°, soluble in alcohol, benzene, acetone, and chloroform with an orange colour, dissolving in glacial acetic acid with a magenta-like red when cold, and becoming orange on boiling the solution. The substance possessed distinctly basic properties, dissolving in hot dilute acids with a fine red colour, and precipitating as an orange crystalline powder on adding alkali to the solution. Preliminary analyses showed that the reaction takes place between one molecule of dibromnaphthol and two molecules of aniline, but the brilliant colour of the base and its salts made it appear highly improbable that the bromine-atoms had been simply exchanged for aniline residues in the sense of the equation—

$$C_{10}H_5Br_2HO + 2H_2N.C_6H_5 = C_{10}H_5HO(NH.C_6H_5)_2 + 2HBr,$$

although the analytical numbers at first obtained agreed very closely with the formula thus required.

A further examination of the compound showed that it was very stable, and that both hydroxyl and amido-groups were probably absent, as it was not attacked by nitrous acid, acetic anhydride, acetyl chloride, or methyl iodide. In its general properties the substance thus agreed entirely with the β-naphthoquinone-dianilide first obtained by Goës (*Ber.*, 1880, p. 123), and described under the name of "diphenyldiimidonaphthol." The same body has been since investigated by Zincke (*Ber.*, 1882, p. 481), who has obtained it among other ways by the direct aniline upon β-naphthoquinone.

The combustions, as already stated, did not at first give satisfactory results, a fact which has been observed by all chemists who have worked with these quinonimide-derivatives. It was not till the substance had been purified by successive crystallisations from alcohol and benzene, that numbers agreeing sufficiently with theory were obtained.

The following are selected from a large number of analyses:—

I. 0·3663 gram gave 1·0819 gram CO_2 and 0·1669 gram H_2O.
II. 0·1764 „ 0·5227 „ 0·0830 „
III. 0·1768 „ 0·5247 „ 0·0825 „
IV. 0·1515 „ 0·4519 „ 0·0691 „
V. 0·1189 „ 0·3531 „ 0·0572 „
VI. 0·1934 „ 0·5780 „ 0·0884 „
VII. 0·2259 „ 18 c.c. N at 18° and 677 mm. bar. = 0·0206 gram N.
VIII. 0·1280 gram gave 9 c.c. N at 16·5° and 768·6 mm. bar. = 0·1060 gram N.

	Theory for $C_{10}H_5(O)(N.C_6H_5)(NH.C_6H_5)$	Found.							
		I.	II.	III.	IV.	V.	VI.	VII.	VIII.
C	81·48	80·55	80·81	80·93	81·35	80·99	81·51	—	—
H	4·93	5·06	5·22	5·18	5·06	5·34	5·07	—	—
N	8·64	—	—	—	—	—	—	9·11	8·28

A specimen of the double zinc salt was prepared by adding zinc chloride solution to a hot solution of the hydrochloride of the base. The salt separates out on cooling in the form of lustrous bronzy scales.

0·1297 gram burnt with lime gave 0·0870 gram AgCl = 0·0215 gram Cl.

	Theory for $[C_{22}H_{16}N_2O,HCl]_2ZnCl_2$.	Found.
Cl	16·56	16·58

The platinum salt, also crystallising in bronzy scales, was prepared in the same manner as the foregoing. It was found necessary to wash this salt with dilute hydrochloric acid as water appeared to decompose it.

I. 0·1460 gram gave 0·0270 gram Pt.
II. 0·1440 „ 0·0266 „

	Theory for $[C_{22}H_{16}N_2O,HCl]_2PtCl_4$.	Found.	
		I.	II.
Pt	18·61	18·49	18·47

The identity of this substance with β-naphthoquinone-dianilide is conclusively established by these results, and the direct passage from a derivative of α-naphthol to a β-naphthoquinone-derivative appears to me to be a reaction of some chemical interest. It appeared at first probable that the compound $C_{10}H_5(HO.....(\alpha))(NH.C_6H_5..(\beta))(NH.C_6H_5..(\alpha))$ might be formed

as the first step in the reaction, this body oxidising under the action of atmospheric oxygen. The leuco-compound in question is easily formed by the action of reducing agents upon the quinone-dianilide, and is of a very unstable character, becoming rapidly oxidised on exposure to the air. The reaction between dibrom-α-naphthol and aniline takes place, however, equally well in an atmosphere of hydrogen, so that this simple explanation of the reaction cannot be maintained. An examination of the alcoholic filtrate obtained by washing the crystalline mass, and after the removal of the excess of aniline by steam distillation, did not show the presence of any appreciably quantity of a bye-product that might have thrown light on the nature of the reaction. The alcoholic filtrate was mixed with caustic soda-solution before distillation so as to decompose aniline hydrobromide and retain any phenolic body present, but nothing was found in the alkaline solution excepting a very small trace of some phenolic compound, crystallising in white scales and too small in quantity to admit of purification or analysis. The test applied showed, however, that this residual compound was not naphthol, and further investigation will be necessary in order to follow the precise course of the reaction. The reduction of the quinone-dianilide is easily effected by means of nascent hydrogen or ammonium sulphide. By titration with a standard solution of stannous chloride, it was found that 2 atoms of hydrogen are taken up in this reduction.*

By the action of dibrom-α-naphthol upon substituted anilines such as parabromaniline, meta- and para-nitraniline, the corresponding derivatives of the quinonedianilide, are obtained, but these have not as yet been examined in detail.

Action upon Toluidine.

On heating dibrom-α-naphthol with orthotoluidine, a reddish-brown colour is developed, but nothing separates out on diluting the contents of the flask with alcohol. The quinone diorthotoluide is certainly formed, but remains in solution.

With paratoluidine the reaction takes place in the same manner as with aniline, the resulting product crystallising either in long silky orange needles or in glistening rhombohedral crystals, orange by transmitted light, and having a metallic green reflection. The needle-shaped crystals appear to be produced by the rapid cooling of the alcoholic solution and the rhombohedra by slow deposition from a weak solution. The melting points were 174—176° (rhombohedra), and 175° (needles).

* I am indebted to my friend Mr. Frank Evershed for making this determination for me. The stannous chloride solution was added to the hot alcoholic solution of the dianilide in presence of a large excess of hydrochloric acid.

The following results were obtained on analysis, the same difficulty of purification having been experienced as in the case of the aniline compound:—

I. 0·1868 gram gave 0·5568 gram CO_2 and 0·1044 gram H_2O.
II. 0·2226 „ 0·6661 „ 0·1179 „
III. 0·2842 „ 18·7 c.c. N at 17·5° and 774·7 mm. bar. = 0·0221 gram N.

	Theory for $C_{10}H_6\langle^{O}_{N.C_7H_7}\rangle NH.C_7H_7$	Found.		
		I.	II.	III.
C	81·81	81·29	81·61	—
H	5·68	6·21	5·88	—
N	7·95	—	—	7·77

The paratoluidine compound closely resembles the aniline derivative in most of its properties.

Action upon Naphthylamine.

Dibrom-α-naphthol, heated with α-naphthylamine, gives a red product containing β-naphthoquinone-di-α-naphthalide, but this compound is freely soluble in alcohol and does not separate out on diluting the product of the reaction with this solvent. With β-naphthylamine a reddish-brown mass is obtained, which on being warmed with alcohol, leaves a reddish crystalline residue. The latter was washed well with alcohol, dried, and then purified by crystallisation from toluene and chloroform successively, the substance being thrown out of the chloroform solution by the addition of alcohol.

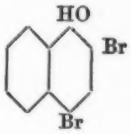
0·2734 gram gave 0·8480 gram CO_2 and 0·1219 gram H_2O.

	Theory for $C_{10}H_6\langle^{O}_{N.C_{10}H_7}\rangle NH.C_{10}H_7$	Found.
C	84·90	84·59
H	4·71	4·95

The β-naphthylamine compound when pure forms a felted mass of dull, reddish, fibrous needles melting at about 246—247°. It possesses but very feeble basic properties, remaining undissolved by boiling dilute acids, and dissolving in hot alcohol only in presence of hydrochloric acid, with a violet colour. The free base is almost insoluble in alcohol, but dissolves in hot toluene or chloroform with a deep reddish-brown colour. Heated with strong sulphuric acid, it forms a readily soluble sulphonic acid.

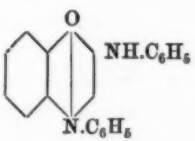
The action of dibrom-α-naphthol upon amines thus furnishes a most simple method of obtaining these quinonimide-derivatives in large

quantities. At the same time their production by this means gives a more direct insight into their constitution than has hitherto been obtained. The constitution of the dibromnaphthol, as might be inferred from analogy with the benzene series,* is most probably—



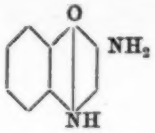
By oxidising some of the substance with an alkaline solution of potassium permanganate in the usual way, a considerable yield of phthalic acid was obtained, thus proving that all three substituents are in the same benzene-ring.

As the precise course of the reactions occurring in the formation of these bodies is still involved in some obscurity, it appeared to me desirable to obtain, if possible, more direct evidence of the constitution of the dibrom-α-naphthol. In former papers (*Ber.*, 1878, p. 1907; *ibid*, 1879, p. 1961) I have shown that when parabromacetnaphthalide is further brominated, the second bromine-atom takes up the ortho-position with respect to the $NH.C_2H_3O$-group. The corresponding dibromnaphthylamine $C_{10}H_5\begin{cases}NH_2\ldots\alpha\\Br\ldots.\beta\\Br\ldots.\alpha\end{cases}$ might thus be expected to be the analogue of dibrom-α-naphthol. An attempt to displace the amido-group in the former compound by hydroxyl by boiling its diazo-sulphate with water, resulted in the formation of a resinous-looking mass, from which, by means of hot alcohol, a small quantity of dibrom-α-naphthol was extracted. The latter was identified by its melting point (111°), and its reaction with aniline. The constitutional formula of dibrom-α-naphthol having been thus established, it follows that the class of bodies represented by β-naphthoquinone-dianilide may be formulated—



Since β-naphthaquinone-dianilide was first obtained by Goës by the action of aniline upon the so-called diimidonaphthol, which Liebermann has shown to be an amidoquinonimide (*Ber.*, 1876, p. 1779), this latter compound may be written—

* This inference has already been drawn by Möhlau, *Ber.*, 1883, p. 2854.



Liebermann's view of the constitution of this body and its derivatives thus receives additional support, and it would perhaps be more correct to speak of β-naphthoquinone-dianilide as phenylamido-α-naphthoquinonephenylimide, and so on throughout the series.

XXV.—*On the Synthesis of Galena by Means of Thiocarbamide, and the Deposition of Lead Sulphide as a Specular Film.*

By J. Emerson-Reynolds, M.D., F.R.S.

Thiocarbamide, or sulphur urea, is now well known to be easily desulphurated by certain metallic oxides and hydrates, notably by those of silver, mercury, and lead. The products, on treatment with a simple oxide, are metallic sulphide, water, and cyanamide—

$$RO + CS(NH_2)_2 = RS + H_2O + CN.NH_2.$$

When free alkali is present the cyanamide soon changes into its polymer, dicyanodiamide. In using the hydrate of lead shortly after I discovered thiocarbamide, it was observed that when the latter was heated with an alkaline solution of lead hydrate, the metallic sulphide sometimes separated in a galenoid form, and became firmly attached as a specular layer to the sides of the vessel.

The best and most uniform results were obtained with a solution prepared by dissolving in 1 litre of water 90 grams of sodium hydrate, and 75 grams of lead tartrate. The caustic soda is first added to about 800 c.c. of water, and the tartrate then digested with the liquid until dissolved, when the solution is made up to the volume of 1 litre. A thiocarbamide solution is prepared by dissolving 17 grams of the amide per litre. This contains more than the necessary proportion of the sulphur compound to secure the complete precipitation of lead as sulphide from an equal volume of the alkaline tartrate solution prepared as above stated.

When a mixture of equal volumes of the two solutions is heated in a beaker, and a thermometer is immersed in the liquid, a brownish coloration appears when the temperature rises to 38—40° C. On continued heating the solution becomes turbid at

about 45°, while at about 50° a specular layer forms at the bottom and sides of the vessel. When the beaker is thoroughly clean in the first instance, the adhesion is uniform and strong. At first the film is thin, and its lustre silvery by reflected light, though brownish by transmission. As the film thickens and loses its translucency it changes colour, and, when opaque, reflects light of the same colour as a brilliant face of a crystal of native galena. The deposition of lead sulphide is gradual, even at the boiling point, in a mixture of solutions of the strength above given, though it is complete after about ten minutes' boiling, and the liquid when filtered is free from any trace of lead. The proportion of the sulphide which attaches itself to the glass surface is small, as I have not found the weight of adherent deposit in the most opaque and strongest films to exceed 2 mgrms. per square centimeter. The excess of sulphide separates as a very dense and easily washed precipitate. The latter when washed and dried possesses the appearance and properties of very finely powdered galena.

The composition of the separated sulphide was sought to be determined by conversion into lead sulphate when oxidised by nitric acid. This method answered tolerably well with small quantities of material, but proved unsatisfactory when several grams were employed, owing to the difficulty in effecting complete oxidation, due to the protective action of the sulphate first formed. Thus in two experiments, while I obtained 1·86 instead of 1·9 grams of $PbSO_4$ in one case, another determination gave only 2·972 grams of $PbSO_4$, instead of 3·14 grams.

The best mode of dealing with the sulphide proved to consist in dissolving a weighed quantity with the aid of heat in just sufficient strong and pure hydrochloric acid to effect complete solution. Hydrogen sulphide is evolved, and the solution of lead chloride is evaporated to dryness and heated carefully over a gas flame, but so as to avoid loss of lead chloride.

2·228 grams of the galenoid sulphide treated in this way gave—

2·594 grams of $PbCl_2$.
Theory (for PbS) requires 2·591 grams.

The slight gain in practice was doubtless due to a trace of sulphur separated in the liquid during decomposition of the sulphide by the acid in presence of air.

Thin brownish films, which have been rapidly formed at comparatively high temperatures, show but little trace of structure when examined under the microscope with a good one-fifth-inch object glass. But strong specular layers which have been less rapidly deposited on smooth surfaces, and exhibit the true galena colour and lustre, are

distinctly granular, like the specimens of compact galena familiar to mineralogists. On the other hand, strong layers which separated on roughened surfaces, very slowly showed numerous minute and brilliant octahedral or tetrahedral faces amongst the apparently granular material; but I have not met with cubic crystals in any of the specimens hitherto produced. It is scarcely necessary to add, however, that octahedral and tetrahedral forms are commonly met with in native galena.*

There is therefore no doubt that the lead sulphide separated by thiocarbamide from the alkaline lead solution is identical with native galena in composition and in general characters, hence a true synthesis of the latter in the moist way has been effected. The ease with which thiocarbamide separates lead sulphide from alkaline solution, suggested the use of the method in ordinary analytical operations. I hope shortly to be able to publish the results of experiments in this direction.

The deposition of galena on glass can take place in the cold as well as when heat is applied, but the process is much slower, and an even layer is not always as easily produced. No evidence of decomposition is obtained for some hours at ordinary temperatures, and the change proceeds very slowly to completion; at low temperatures several days may elapse before all the lead sulphide has separated. As might be anticipated, deposition is more rapid from concentrated than from dilute solutions.

Articles immersed in liquids from which galena is in process of separation, receive, if clean, strongly adherent coatings, which can withstand considerable friction with a wash-leather, and under this treatment take a fine polish.

The process of plating† glass articles with galena is best conducted in warm liquids. The vessels may be plated externally or internally, in the latter case polishing is of course unnecessary.

In the same way galena can be deposited on porcelain and on ebonite or other material not much acted upon by the alkaline liquid. Iron and steel surfaces, if perfectly clean, take good deposits, but the

* It seems to be necessary to point out that the term "galena" is applied by mineralogists not only to distinct crystals of native lead sulphide, but also to "tabular, coarse or fine granular, sometimes impalpable" forms of the mineral (see Dana, 5th edition, p. 40), provided only that the specimens exhibit the leaden colour and lustre of the crystalline mineral, as distinguished from the brown-black and almost lustreless sulphide, commonly precipitated by hydrogen sulphide from lead solutions. On precisely the same grounds the compound separated from alkaline lead solutions by thiocarbamide would be correctly termed galena, even if I had not found it to be capable of assuming crystalline forms.—J. E. R.

† The process was protected, but the patent rights have been allowed to lapse.

adhesion of the galena to the metal is not sufficiently strong to render the layer wear resisting.

Brass can be easily plated if the proportion of caustic soda in the lead solution be increased by one-half, and the highly polished metal be immersed in the warm mixture, when the sulphide has just began to separate. The temperature should then be quickly raised to the boiling point. If the metal be examined from time to time, the surface will be found to change from a fine rosy-red colour to rich indigo-blue, and then to silver-white. If the article be removed at this point, washed and polished, it appears as if nickel plated, but this fine surface easily oxidises, especially in a damp atmosphere. If, however, the article be not withdrawn but boiled in the liquid for some minutes, the true galena coating is formed, which polishes well to a fine lead-blue colour, and can withstand moderate friction. In a very damp atmosphere or one containing ozone, chlorine, &c., the polish of the surface of galena is affected, but is easily restored by friction with leather, which treatment, however, involves some loss of material.

When once thiocarbamide can be produced at a sufficiently cheap rate, galena plating may be applied to many useful purposes; but the existing patent rights controlling the production of ammonium thiocyanate, from which thiocarbamide is produced, prevent at present the use of the latter in quantity.

XXVI.—*On the Critical Temperature of Heptane.*

By T. E. Thorpe and A. W. Rücker.

In a paper on heptane from *Pinus sabiniana* (Thorpe, Trans., **35**, 296), one of us gave the results of a number of determinations of the physical characters of this hydrocarbon, and among them the details of a complete series of measurements of its superficial tension, as obtained from observations on its rise in a cylindrical capillary tube of known diameter. These experiments were so arranged that the relation of the surface-tension to the temperature could be ascertained by observing the rise of the liquid in the same tube at different temperatures in an apparatus specially devised for measurements of this nature.

The surface-tension of this heptane in C.G.S. units at 0° was found to be 22·19, and its relation to temperature was very accurately represented by the expression $T = 22{\cdot}19\ (1 - 0{\cdot}003563t)$.

Since the superficial tension of a liquid vanishes at the temperature at which the gaseous and liquid states become continuous, that is at the critical temperature, the expression $1-0{\cdot}003563t$ affords us the means of calculating approximately the critical point of heptane. It was thus found to be 281° (*loc. cit.*, p. 308).

Since the date of this paper it has been shown that heptane from *Pinus sabiniana* is the normal hydrocarbon (Schorlemmer and Thorpe, *Phil. Trans.*, 1883).

In a series of papers, abstracts of which have appeared in this Journal (Abstr. for 1883, 276; 1884, 252), Pawlewski has published a large number of determinations of the critical temperatures of liquids, organic and inorganic, from which certain important deductions may be drawn. Thus it appears that there is a constant difference between the critical temperature and boiling points of strictly homologous compounds. In the case of the alkyl salts of the $C_nH_{2n}O_2$ series, this difference amounts to 182·3°. This value was obtained from 17 substances, and the individual numbers in no case differed by more than 0·5 per cent. from the mean. In the fatty acid series the difference amounts to about 202°; in the ethylene series it is about 163°. Among the normal hydrocarbons of the C_nH_{2n+2} series, the only example given by Pawlewski is that of hexane, of which the boiling point is 68°, and for which the critical temperature was found to be 250·3°, or a difference of 182·3°, exactly the same, as it happens, as that which obtains among the alkyl salts of the fatty acid series.

On the assumption that what is found to hold good in the case of other homologous series is equally true in that of the paraffins, we have now the means of controlling the value of the determination of the critical point of normal heptane, as deduced from the law of the decrease in its capillarity by temperature.

It was found that normal heptane under the standard pressure boiled at 98·4°. This number, added to Pawlewski's constant, 182·3°, affords 280·7° as the critical temperature of this hydrocarbon. The number deduced from the observations on superficial tension was 281°.

We may take this opportunity of stating that we have been engaged for some time past in measuring the superficial tensions of liquids with special relation to temperature, with the view of determining the connection between this factor and their critical points and the law of their thermal expansions.

XXVII.—*On Scovellite.*

By W. N. Hartley, F.R.S.E., Royal College of Science, Dublin.

On page 26 of the *Journal of the Chemical Society*, in the January number of this year, is an abstract of a paper "On Scovellite, a new Phosphate of Didymium, Yttrium, and other rare Earths, from Salisbury, Conn., by George J. Brush and Samuel L. Penfield." The description, short though it is, seems to indicate that scovellite must be a variety of rhabdophane, a mineral which was analysed by me. (*Chem. Soc. J.*, **41**, 210, Trans., 1882.) In order to examine this matter more thoroughly, I have referred to the original paper (*Amer. J. Sci.*, **25**, 459), and the description there given tallies exactly with the physical properties of rhabdophane. In chemical composition it differs (1) in containing a considerable quantity of a carbonate of lanthanum, which, if reckoned as lanthanite, $R_2(Ce_2)_3,9H_2O$, amounts to 17 per cent.; (2), in the absence of cerium; (3), in the presence of a considerable quantity of erbium. Rhabdophane has the formula $R_2(PO_4)_2,2H_2O$, where R may be Ce, La, Di, or Yt, the four metals wholly or in part replacing each other. It retains water at a high temperature, it loses very little at 150°, and at 200° cannot be dehydrated even after repeatedly heating for several consecutive hours; by ignition only can it be dehydrated.

Scovellite loses 1·5 per cent. of water at 100°, it is therefore not improbable that it may contain between 14 and 15 per cent. of a carbonate (La, Di), $O_3.3CO_2.3H_2O$; the proportion of water combined with the lanthanum carbonate, which is driven off at 100°, being in accordance with this view.

Messrs. Brush and Penfield give two formulæ for the carbonate and the phosphate, as derived from their analyses, which are the following:—

(1.) $R_2O_3,3CO_2,9H_2O$
$R_2(PO_4)_2,H_2O.$

(2.) $R_2O_3,3CO_2,3H_2O$
$R_2(PO_4)_2,2H_2O$, nearly.

They prefer the former of these because, as they say, the carbonate may be regarded as lanthanite. If we adopt the latter, the phosphate, which is the chief constituent of the mineral, has the constitution of rhabdophane, and it may be regarded as an erbium-yttrium variety of that mineral associated with a lanthanum carbonate, which, containing 10·5 per cent. of water, resembles a Swedish specimen of

lanthanite analysed by Hisinger, which contained 13·5 per cent. (*Dana and Brush's Mineralogy*, p. 710, 5th edition, 1874).

My attention has been directed to a paper published in the *American Journal of Science* for March, 1884, the title of which is "On the Identity of Scovellite with Rhabdophane." I have not the advantage of being able to refer to this publication at the present moment, but having perused it I am happy to state that the views of Professor Brush and Mr. Penfield coincide with my own. They express regret that, at the time their memoir was written, they were not acquainted with the analysis and formula for rhabdophane given by me. As rhabdophane is a very rare mineral, it is extremely interesting to hear of its discovery in the United States, and particularly so as we may expect now to be informed of other localities for it.

XXVIII.—*Analysis of Woodall Spa.*

By W. T. Wright, Student in the Firth College, Sheffield, and T. Burton, Student in University College, Dundee.

The Spa of Woodall in Lincolnshire, about midway between Lincoln and Boston, is much esteemed for its medicinal virtues, especially in cases of gout, rheumatism, epilepsy, enlarging tumours, skin diseases, &c., its properties being due in great measure to the iodine and bromine which it contains, the proportions of these elements being indeed greater in this Spa than in those of Leamington and Harrogate.

The water comes into the well at a depth of 50 feet from the surface of the ground; for analysis it was collected at a depth of 170 feet.

In the following table of analytical results (I) is the analysis of the water collected by us on April 23rd, 1883. (II) is Dr. Frankland's analysis made in 1875:—

Height above sea level.....	About 16 feet.
Temperature of external air ..	1·7° C.
„ „ water	15·6 „
Specific gravity at 15·5° C.	1·009177

	I. (Pts. per million).	II. (Pts. per million).
Total solids at 100° C.	20,200·000	23,612·000
„ „ after ignition	18,200·000	—
Temporary hardness	125·557	200·000
Permanent „	1,842·800	2,450·000
Organic carbon	—	3·720
Organic nitrogen	—	5·320
Ammonium (NH_4)	6·032	8·577
Albuminoid ammonia	0·712	—
Nitrogen as nitrate and nitrites	—	0·090
Total combined nitrogen	—	12·080
Silica	26·457	—
Calcium	549·642	—
Magnesium	279·972	—
Iron	1·300	—
Sodium	6,089·290	—
Potassium	45·652	—
Aluminium	7·643	—
Chlorine	11,113·737	14,250·000
Bromine	49·729	62·800
Iodine	5·216	8·800
Sulphate	111·504	—
Carbonate, small, not exceeding	68·541	—
Arsenic	nil	0·160

Gases:—

Total gases	50·413 c.c. per litre
Carbon dioxide	27·414 „
Oxygen	3·491 „
Nitrogen	19·508 „

The above, in combination, may be represented as follows:—

Calcium sulphate	157·964 pts. per mil.
Calcium chloride	1,396·330 „
Magnesium iodide	5·709 „
Magnesium bromide	57·188 „
Magnesium chloride	1,076·746 „
Aluminium chloride	37·790 „
Potassium chloride	87·157 „
Sodium chloride	15,398·207 „
Sodium silicate	53·796 „
Ferrous carbonate	2·693 „
Sodium bicarbonate	128·900 „

With reference to the method of analysis it is only necessary to state that the chlorine, bromine, and iodine, were estimated by A. Guyard's method (*Bull. Soc. Chim.* [2], **31**, 301—302).

The total gases contained in the water are equal to about the average quantity held in mineral waters.

The number of springs, either in England or abroad, containing iodine and bromine, is very small. The following is a list of those which contain most iodine and bromine of any yet published:—

	Iodine, parts per million.	Bromine, parts per million.	Analyst.
Woodall Spa	5·216	49·729	Burton and Wright.
Leamington	1·429	5·714	
Old Sulphur Well, Harrogate	1·460	28·050	(Thorpe).
Kreuznach	1·786	35·720	
Aix-la-Chapelle	0·400	2·700	(Liebig).
Casteggio, Italy	4·865	42·480	
Challes, in Savoy	10·450	2·920	
Mineral springs of Java	116·800	—	E. Reichardt.

From the above it will be seen that Woodall Spa is much richer in these elements than any other spring in England, whilst of European spas, those of Casteggio in Italy and of Challes in Savoy, are the only two which rival it in this respect.

XXIX.—*On Benzoylacetic Acid and some of its Derivatives.* Part I.

By W. H. Perkin (Jun.), Ph.D., Privatdocent at the University of Munich.

Among the many methods which have been discovered and employed in the last few years, for the synthesis of organic compounds, those which are based on the use of acetoacetic ether are among the most important, this body being useful in two ways for building up organic bodies: in the first place on account of the acid character of the hydrogen-atoms contained in the methylene-group; and in the second place, being a ketone, it is capable of entering into almost all the reactions which characterise the latter class of bodies. The replacement of the hydrogen-atoms in acetoacetic ether, by alcohol and acid radicals, has been especially studied by Wislicenus and his pupils;

whereas the reactions which involve the ketone-group have, with few exceptions, been more or less neglected.

The reason of this is that not only are the experimental difficulties great, but there is also considerable uncertainty in interpreting the results, owing to the mobility of the different groups in acetoacetic ether. More especially does doubt exist as to the part played by the methyl-group in such reactions and condensations. For this reason it appeared to me that it would be very interesting to carefully examine the benzoylacetic ether, recently discovered by Baeyer (*Ber.*, **15**, 2705), with especial reference to reactions in which the ketone-group takes part. Benzoylacetic ether, as was to be expected, gives in the aromatic series bodies exactly corresponding to those obtained from acetoacetic ether in the fatty series, and for this reason, as well as on account of the stability of the benzoyl-group, and the greater tendency of bodies in the aromatic series to crystallise, it seemed to be especially adapted to the study of the more complicated condensations.

Before entering into the details of this research, I should like to express my sincere thanks to Professor Baeyer, in whose laboratory it was carried out, for his kind help and advice which he always placed at my disposal during its progress, as well as for the interest which he took in all my other studies. I must also thank Herr C. Bernhart for the help which he gave me in the experimental part.

Part I of this research comprises the preparation and properties of benzoylacetic ether, benzoylacetic acid, and the compounds in which the hydrogen-atoms in the methylene-group are replaced by alcohol radicals.

Preparation of Phenylpropiolic Acid.

Cinnamic acid, as is well known, combines directly with two atoms of bromine, being thereby converted into phenyldibromopropionic acid, thus:

$$C_6H_5.CH : CH.COOH + Br_2 = C_6H_5.CHBr.CHBr.COOH.$$

This acid, on treatment with alcoholic potash, first gives up 1 mol of hydrobromic acid, forming the two isomeric α- and β-monobromocinnamic acids according to the equation—

$$2C_6H_5CHBr.CHBr.COOH = \underset{\alpha\text{-Monobromocinnamic acid.}}{C_6H_5CBr : CH.COOH} + \underset{\beta\text{-Monobromocinnamic acid.}}{C_6H_5CH : CBr.COOH} + 2HBr.$$

By converting these acids into ammonia salts and recrystallising once or twice from water, it is easy to separate the one from the other, the ammonia-salt of α-monobromocinnamic acid being much less soluble than that of the β-acid. Of these two bodies only the α-acid gives a good yield of phenylpropiolic acid on treatment with alcoholic potash, the β-acid being partly transformed into monobromostyrolene and other secondary products (Barisch, *J. pr. Chem.* [2], **20**, 180; Glaser, *Annalen*, **154**, 140). It is therefore necessary before heating with potash, to transform the β-acid into the α-acid, which is easily done by heating it some degrees above its melting point, or more simply still by etherification, in which case the ether of the α-acid is formed. The formation of phenylpropiolic acid from α-monobromocinnamic acid is represented by the following equation:—

$$C_6H_5.CBr:CH.COOH = C_6H_5.C:C.COOH + HBr.$$

After many experiments, however, it was found that the following modification of the above process gives the best results, at the same time rendering the somewhat troublesome transformation of the β- into the α-monobromocinnamic acid unnecessary.

500 grams of cinnamic acid are suspended in about 1—1½ litres of absolute alcohol, and hydrochloric acid is passed through till the whole is dissolved and the liquid is thoroughly saturated with the gas. The product, after standing for two or three hours, in order to make sure that the reaction is complete, is poured into ice and water, and the oil which sinks to the bottom is separated by means of a tap-funnel, the watery liquid being extracted with a little ether. This oil, which consists of almost pure cinnamic ether, is next dissolved in a little ether, washed with a dilute solution of sodium carbonate, to remove traces of hydrochloric acid and unchanged cinnamic acid; and after thoroughly drying over chloride of calcium, treated with 440 grams of bromine, in small quantities at a time, care being taken to keep the liquid cool. The bromine disappears instantly without evolution of hydrobromic acid. After standing for a short time, the whole is poured into a large open dish and the ether is allowed to evaporate, when phenyldibromopropionic ether separates out in large crystals, forming a solid cake at the bottom of the dish. The crystals are then separated from the mother-liquor, pressed between filter-paper, exposed to the air for a short time to remove traces of bromine, and lastly, if necessary, crystallised from ligroin or alcohol.

The mother-liquor on evaporation deposits crystals of the ether, which are somewhat discoloured by impurities, but on recrystallisation may easily be obtained pure, and melting at 69°.

A weighed quantity of this body is now added to the calculated

quantity of alcoholic potash (1 mol. of ether requires 3 mols. of potash). The reaction is so energetic that the heat evolved is generally sufficient to cause the alcohol to boil. As soon as all the ether has been added, the whole is heated to boiling for six to eight hours in a flask connected with an inverted condenser. After distilling off the alcohol, the residue, which consists of a mixture of potassic phenylpropiolate and potassic bromide, is dissolved in water and filtered, and the clear liquid is acidulated with an excess of dilute sulphuric acid, which precipitates the phenylpropiolic acid as an oil, which, however, on standing, soon solidifies, especially if well agitated from time to time. The crude acid is next filtered off, well washed with water, dissolved in carbonate of soda solution, and gently heated with animal charcoal for about half an hour on a water-bath, agitating well from time to time. After filtering off the animal charcoal, an almost colourless solution of soda-salt is obtained, which, on acidulating with sulphuric acid, deposits the phenylpropiolic acid nearly pure. If required perfectly pure, it must be crystallised from water, and is thus easily obtained in well-characterised crystals, which Professor Haushofer was kind enough to measure, and describe as follows :—

Phenylpropiolic Acid.

"Prismatic crystals of the rhombic system with monoclinic habit. Acute dihedral angle of the prism 66° 50′. Of pyramidal faces, there appear constantly only the pair resting on an obtuse edge of the prism. Very characteristic is the twin-combination of the crystals according to the macropinacoid, whereby the hemi-pyramids of the two individuals are symmetrically joined, and form re-entering angles. The entire development of the crystals is so decidedly monoclinic, that my reference of them to the rhombic system is based solely on the directions of extinction on the prismatic faces, which directions are exactly parallel and perpendicular to the prismatic edges."

Phenylpropiolic acid is produced from the dibromophenylpropionic ether according to the following equation :—

$$C_6H_5.CHBr.CHBr.COOC_2H_5 + 3KOH = C_6H_5.C:C.COOK + 2KBr + 2OH_2.$$

By this method there is apparently no bromstyrolene formed, and if care be taken to avoid any large excess of potash in saponifying the dibromophenylpropionic ether, the yield is very good, about 80—85

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per cent. of the theoretical amount. If, however, excess of potash be used, the phenylpropiolic acid is easily decomposed into phenylacetylene and acetophenone.

Preparation of Benzoylacetic Ether.

The phenylpropiolic acid must now be converted into the ethylic ether, which is best done in the following way. Pure phenylpropiolic acid is dissolved in absolute alcohol, and hydrochloric acid gas is passed through the liquid till the whole is thoroughly saturated, care being taken to cool the liquid well during the operation, after which the product is left at rest for two or three hours in order to complete the reaction. The whole is then poured into ice-cold water, and the phenylpropiolic ether, which is precipitated as an oil, is two or three times extracted with ether.

The etheric solution, after washing with dilute carbonate of soda, is well dried over chloride of calcium and the ether is distilled off, when pure phenylpropiolic ether remains behind as a thick, and almost colourless oil, having a fruity smell and burning taste; it does not solidify at 0°. If rubbed on the skin it produces a most painful burning sensation. When quickly distilled it boils between 260° and 270° without undergoing much decomposition. When this ether is dissolved in common sulphuric acid it takes up the elements of water, forming ethylic benzoylacetate, thus:—

$$C_6H_5.C:C.COOC_2H_5 + H_2O = C_6H_5.CO.CH_2.COOC_2H_5.$$

For the formation of benzoylacetic ether in this way, commercial sulphuric acid is somewhat too concentrated, and a better yield is obtained if a few drops of water are added to every kilogram before use.

The method of preparation is the following:—From 2 to 3 kilos. of sulphuric acid are cooled to 0° in a freezing mixture, and then 100 grams of phenylpropiolic ether are slowly added, drop by drop, so that the temperature never rises above + 3°, the whole being well shaken after each addition. The sulphuric acid becomes coloured slightly brownish during the reaction, and there appears always to be a little sulphurous anhydride formed, especially if a rise of temperature takes place. After standing for two or three hours at as low a temperature as possible, the product is slowly poured on powdered ice, everything being carefully cooled, and the operation being best performed by allowing the sulphuric acid to trickle into a funnel filled with ice, which is kept well stirred all the time. The watery liquid, which is filled with drops of oil, is repeatedly extracted with ether.

The etheric solution is then quickly washed with a dilute solution of sodium carbonate, and finally dried over potassium carbonate, which, as a rule, extracts a quantity of colouring matter. After filtering from potassium carbonate and distilling off the ether, crude benzoylacetic ether remains behind as a thick yellowish oil.

In order to purify this liquid, it is next shaken with a cold dilute solution of caustic soda and a little animal charcoal, and filtered, the whole operation being performed as quickly as possible, in order to avoid decomposition of the ether. The clear alkaline solution is next mixed with ice, acidulated with dilute sulphuric acid, and well shaken with ether; and lastly this etheric solution is carefully dried over potassium carbonate, and the ether distilled off, when pure benzoylacetic ether remains behind as a colourless oil, which can easily be freed from traces of ether by leaving it for some time over sulphuric acid in a vacuum.

On analysis the following numbers were obtained:—

I. 0·2072 gram substance gave 0·1198 OH_2 and 0·5208 CO_2.

	Found.	Theory, $C_6H_5.CO.CH_2COOC_2H_5$.
C =	68·62 per cent.	68·75 per cent.
H =	6·42 „	6·25 „
O =	24·96 „	25·00 „

Benzoylacetic ether is a colourless oil having an agreeable smell, somewhat recalling that of acetoacetic ether. It does not solidify at 0°. If quickly fractioned most of it distils over between 265° and 270° without much decomposition. Under a pressure of 200 mm. it passes over between 230° and 235°. It should not, however, be distilled, if this operation can be avoided, as it entails considerable loss, and the crude ether is generally pure enough for most purposes.

Benzoylacetic ether is sparingly soluble in water, but mixes with ether and alcohol in all proportions. The solution in alcohol gives the same violet coloration with chloride of iron as acetoacetic ether. By boiling with water, or better with dilute sulphuric acid, it is split up into acetophenone, alcohol, and carbonic anhydride, according to the equation:—

$$C_6H_5.CO.CH_2.COOC_2H_5 + H_2O = C_6H_5CO.CH_3 + CO_2 + C_2H_5OH.$$

This decomposition is exactly analogous to the splitting up of acetoacetic ether into acetone, alcohol, and carbonic anhydride. In benzoylacetic ether, just as in acetoacetic ether, the hydrogen-atoms in the CH_2-group are replaceable by sodium. It appears, however, that after having replaced 1 atom of hydrogen with sodium, it is necessary

first to exchange this for some radical such as ethyl, before it is possible to insert another.

The sodium-compound is best prepared by mixing benzoylacetic ether (4 grams) with a strong solution of sodium ethylate in alcohol, containing the calculated quantity of sodium (0·6 gram). The reaction takes place according to the equation :—

$$C_6H_5.CO.CH_2.COOC_2H_5 + NaOC_2H_5 = C_6H_5.CO.CHNa.COOC_2H_5 + C_2H_5OH.$$

After standing for some time in the dark, the sodium-compound crystallises out in long silky needles which, however, on being exposed to the air, quickly turn brown, especially when moist.

The mother-liquor is then drawn off by means of a vacuum pump, and the crystals are pressed between filter-paper, when the sodium-compound is obtained pure, having somewhat the appearance of cotton wool. On standing in contact with the air, however, it slowly decomposes. If heated in the dry state it decomposes easily, yielding acetophenone and other bodies. It is readily soluble in water and alcohol, almost insoluble in ether.

The following derivatives of benzoylacetic ether were prepared by precipitation from a solution of the sodium-compound in water.

The *barium compound*, $(C_{11}H_{11}O_3)_2Ba$, is precipitated on adding barium acetate as a white amorphous mass, sparingly soluble in water, but more so in alcohol.

The *silver compound*, $C_{11}H_{11}AgO_3$, is formed by adding a solution of silver nitrate. It is a white amorphous precipitate. On warming, silver is immediately precipitated; it is also easily decomposed by caustic soda.

On adding copper sulphate to the solution of the sodium salt, the *copper compound*, $(C_{11}H_{11}O_3)_2Cu$, is precipitated as a pale green mass, insoluble in water. In dilute soda solution it dissolves easily, forming a beautiful blue solution, from which CuO is precipitated on boiling.

The *lead compound* is precipitated, on adding lead acetate, as a white precipitate, which is also soluble in caustic soda.

Ferric chloride gives a dirty violet coloration with dilute solutions of the sodium salt, the liquid becoming turbid on standing.

Benzoylacetic Acid.

Some time since Ceresole (*Ber.*, **15**, 1871), by saponifying acetoacetic ether with dilute potash at ordinary temperatures, obtained the corresponding acetoacetic acid. It therefore appeared interesting to

see if in this case, by saponification in the cold, benzoylacetic acid could be isolated, this appearing the more probable, as benzoylacetic ether is more stable than acetoacetic ether. Pure benzoylacetic ether was therefore dissolved in dilute aqueous potash ($2\frac{1}{2}$—3 per cent.), care being taken to avoid any large excess, and then left at rest at the ordinary temperature for about 24 hours. The product was then filtered, and after carefully cooling with ice, acidulated with dilute sulphuric acid, when the acid was precipitated in white flakes. After extracting with ether, the etheric solution was allowed to evaporate at the ordinary temperature, the acid remaining behind as a slightly brownish, hard, crystalline mass, which was next dissolved in dilute ammonia, shaken with a little animal charcoal, and filtered.

On acidulating with dilute sulphuric acid, and extracting with ether, the acid remained as an almost colourless crystalline mass, consisting of nearly pure benzoylacetic acid.

In order to obtain the body perfectly pure, it is dissolved in a little warm benzene (at 70°), and a trace of light petroleum added. On cooling, the acid crystallises out in small crystals, which, when seen under the microscope, appear in the form of thin transparent needles, which polarise light. The analysis gave the following numbers:—

I. 0·1519 gram substance gave 0·0675 gram OH_2 and 0·3647 gram CO_2.

II. 0·1492 gram substance gave 0·0695 gram OH_2 and 0·3614 gram CO_2.

	Found.		Theory,
	I.	II.	$C_6H_5.CO.CH_2.COOH$.
C =	65·48	66·06 per cent.	65·85 per cent.
H =	4·93	5·17 „	4·88 „
O =	29·59	28·77 „	29·27 „

Benzoylacetic acid, several times crystallised from benzene, melts at 103—104°, if quickly heated, at the same time undergoing decomposition, with evolution of carbonic anhydride. (The melting point, 85—90°, first given in the *Berichte* [**16**, 2129], is too low, owing to the fact that at that time I had not sufficient substance at my disposal to purify it by repeated crystallisation.)

The acid appears to sublime slowly at ordinary temperatures, so that if preserved in a test-tube the sides, after some months, become covered with thin colourless transparent plates, consisting, apparently, of pure benzoylacetic acid. This acid is difficultly soluble in light petroleum, and crystallises from the hot solution on cooling in small flat needles. It is easily soluble in alcohol, ether, and hot benzene. On adding light petroleum to the solution in benzene the acid is almost completely precipitated in the form of slender needles

A small crystal of the acid dissolved in alcohol gives, on addition of a drop of ferric chloride, a beautiful reddish-violet coloration.

Benzoylacetic acid is sparingly soluble in cold water, the solution giving only a slight coloration on adding chloride of iron; it is much more easily soluble in hot water, a drop of chloride of iron producing an intense violet coloration.

Benzoylacetic acid may be formed directly, by dissolving finely powdered phenylpropiolic acid in concentrated sulphuric acid, according to the equation—

$$C_6H_5.C\vdots C.COOH + H_2O = C_6H_5.CO.CH_2.COOH.$$

When the acid liquid is poured on ice, a yellow amorphous mass is obtained consisting of benzoylacetic acid, mixed with a little unchanged phenylpropiolic acid.

The former acid, on heating either alone or with dilute sulphuric acid, is quantitatively decomposed into acetophenone and carbonic anhydride, thus:—

$$C_6H_5.CO.CH_2.COOH = C_6H_5.CO.CH_3 + CO_2.$$

The formation of acetophenone, by the action of concentrated potash on phenylpropiolic acid, is probably due to the latter first taking up the elements of water, being thereby converted into benzoylacetic acid, which is then decomposed by the further action of the alkali into potassium carbonate and acetophenone.

Benzoylacetic acid dissolves easily on shaking with dilute soda, sodium carbonate, or ammonia. In order to prepare the silver salt, the acid was dissolved in dilute ammonia, and the solution, after filtering, left over sulphuric acid in a vacuum till the excess of ammonia had volatilised, or, better still, carefully neutralised with pure nitric acid. On adding a solution of silver nitrate, the silver salt was precipitated in the form of a white amorphous mass, somewhat soluble in water. It was filtered off, well washed, and dried over sulphuric acid in a vacuum. The analysis gave the following numbers:—

0·1440 gram substance gave 0·0567 gram silver.

Found.	Theory, $C_6H_5CO.CH_2.COOAg$.
Ag = 39·37 per cent.	39·77 per cent.

The silver salt is instantly decomposed on heating, with separation of silver.

The following salts were prepared from the ammoniacal salt, which can be obtained as a waxy crystalline mass, by allowing the aqueous

solution to evaporate to dryness in a vacuum over sulphuric acid. The crystals are generally mixed with traces of acetophenone, produced by the spontaneous decomposition of the salt. The ammonium salt is easily soluble in water. On adding *ferric chloride* to a solution of the ammonium salt, a thick blackish-violet precipitate is formed, which is slowly decomposed on boiling, carbonic anhydride being evolved. *Ferrous sulphate* does not give any precipitate. The *copper salt* is produced by adding a solution of copper sulphate to a fairly concentrated solution of the ammonium salt, as a light greenish-yellow precipitate, which is not formed in dilute solutions. It is fairly stable, but is slowly decomposed on boiling.

The *lead salt* is precipitated, on adding acetate of lead, as a heavy white amorphous precipitate. The calcium and barium salts are easily soluble in water.

The salts of benzoylacetic acid are difficult to obtain pure and to analyse, on account of their tendency to decomposition into acetophenone and carbonic anhydride. From the above facts it is evident that benzoylacetic acid, although not a stable body, is much more so than acetoacetic acid, which has never been obtained pure enough for direct analysis.

Ethylbenzoylacetic Acid.

It was now necessary to see whether it was really possible, as in the case of acetoacetic ether, to replace the hydrogen atoms in the methylene-group, by alcohol-radicals, such as methyl, ethyl, &c., and thus to obtain higher homologues of benzoylacetic acid. The first experiment tried was the action of ethyliodide on the sodium-compound of benzoylacetic ether, in the hope of getting ethylbenzoylacetic ether, according to the following equation:—

$$C_6H_5.CO.CHNa.COOC_2H_5 + C_2H_5I = C_6H_5 + CO.CH(C_2H_5).COOC_2H_5 + NaI.$$

The method of procedure was the following:—

0·6 gram of sodium was dissolved in about 15 c.c. of absolute alcohol, and then mixed with 5 grams of pure benzoylacetic ether, taking care to avoid any rise of temperature. 10 grams of ethyliodide were then added, and the whole heated on a water-bath till a sample, on dilution with water, had no longer an alkaline reaction. The alcohol and excess of ethyliodide were then distilled off, the residue mixed with water, and the oily product extracted with ether. The etheric solution, after well washing and drying over carbonate of potash, left, on distilling off the ether, a thick yellowish oil, consisting probably of nearly pure ethylbenzoylacetic ether, which was,

however, not further examined, as it appeared to be decomposed on distillation. In order to obtain the free acid, the oil was mixed with dilute alcoholic potash and left for several days at the ordinary temperature until, on diluting a sample with water, only a small quantity of oil was precipitated. The product was mixed with water and several times extracted with ether, to remove any unchanged ethylic ethylbenzoylacetate. The solution of the potash salt of the new acid was then acidulated with dilute sulphuric acid, a solid acid being thereby precipitated, which was extracted with ether. After distilling off the ether, the acid remained behind as a semi-solid mass, which was first spread on a porous plate to remove traces of oil, and then purified by dissolving it in a small quantity of dilute alcohol, from which solvent it crystallises in small needles.

After drying at 60° the following numbers were obtained on analysis :—

0·1914 gram substance gave 0·1082 H_2O and 0·4814 CO.

	Found.	Theory, $\begin{matrix}C_6H_5CO\\C_2H_5\end{matrix}\!>\!CH.COOH$.
C =	68·60 per cent.	68·75 per cent.
H =	6·28 „	6·25 „
O =	25·12 „	25·00 „

It was therefore ethylbenzoylacetic acid. The acid melts at 111—115° with slight decomposition, but could not be obtained free from traces of benzoic acid, which, while rendering it difficult to get an accurate melting point, do not much influence the analytical results. It is easily soluble in alcohol, ether, and benzene, and crystallises on evaporating the etheric solution in silky needles; it is easily soluble also in ammonia, soda, and sodium carbonate solution. When warmed with dilute sulphuric acid, it is decomposed, carbonic acid being given off, and an oil remaining behind, probably consisting for the most part of ethylacetophenone.

Decomposition-products of Ethylbenzoylacetic Ether.

It next appeared interesting to determine whether the substituted benzoylacetic ethers would, on heating with alcoholic potash, undergo the same decompositions as the corresponding substituted acetoacetic ethers, which, as is well known from the researches of Wislicenus, are split up in two ways. He found, namely, that on employing a highly concentrated potash solution, the product consisted chiefly of organic acids, whereas with dilute solutions a large amount of ketone and

only a small quantity of organic acids were obtained, according to the following equations, taking ethylacetoacetic ether as example:—

I. $CH_3.CO.CH(C_2H_5).CO_2C_2H_5 + 2KOH = CH_3.CO_2K +$ Butyric acid. $C_2H_5.CH_2CO_2K + C_2H_5OH.$

II. $CH_3.CO.CH(C_2H_5).CO_2C_2H_5 + 2KOH = CH_3.CO.CH_2.C_2H_5 +$ Methylpropyl ketone. $C_2H_5OH + K_2CO_3.$

As will be seen from the following remarks, this rule applies also to the substituted benzoylacetic ethers.

In order to examine the decomposition-products of ethylbenzoylacetic ether, the crude ether was heated on a water-bath for three hours with moderately concentrated alcoholic potash. The mixture quickly became deep brown, and acquired a smell strongly resembling that of acetophenone. At the end of the reaction water was added, and the precipitated oil was separated from the potash-salt, by extraction with ether.

The etheric solution, after well washing with water, and drying with carbonate of potash, gave, on distilling off the ether, a dark brownish oil, which was then carefully fractioned. Almost the whole quantity distilled over by the first distillation, between 215—230°, and gave, on oft-repeated fractioning, an oil, boiling constantly by 220—222°.

The analysis gave the following results:—

0·1588 gram substance gave 0·1140 gram H_2O and 0·4687 CO_2.

	Found.	Theory, $C_6H_5.CO.CH_2.C_2H_5$.
C =	80·49 per cent.	81·08 per cent.
H =	7·97 „	8·10 „
O =	11·54 „	10·82 „

Propylphenylketone had therefore been formed from the ethylbenzoylacetic ether by splitting off CO_2 and alcohol, according to the following equation:—

$$C_6H_5.CO.CH(C_2H_5)COOC_2H_5 + 2KOH = C_6H_5.CO.CH_2.C_2H_5 + C_2H_5OH + K_2CO_3.$$

This ketone has already been described by Schmidt and Fieberg (*Ber.*, **6**, 498), and by Burcker (*Bull. Soc. Chim.*, **37**, 4). The former obtained it by the distillation of a mixture of benzoate and butyrate of lime, the latter by the action of aluminium chloride on butyric chloride and benzene.

It does not combine with sodium bisulphite. On oxidation with chromic acid and sulphuric acid benzoic and propionic acids are formed.

In order to examine the acids produced by the action of potash on ethylbenzoylacetic ether, the potassium salt which had been separated from the propylphenylketone, by extraction with ether, was next acidulated with dilute sulphuric acid, and distilled with steam. An almost colourless but strongly acid liquid distilled over, which possessed strongly the characteristic smell of butyric acid. The residue on cooling was extracted with ether.

On distilling off the ether a solid acid remained behind, which crystallised from water in silky plates, possessing all the properties of benzoic acid. They melted at 120°, and sublimed very easily on heating, and gave the characteristic iron reaction: in order to be certain the acid was turned into the silver salt and analysed with the following result:—

0·4026 gram substance gave 0·1917 gram Ag = 47·59 per cent.
Theory for C_6H_5COOAg = 47·16 „

By the action of potash on ethylbenzoylacetic ether, a second decomposition had therefore taken place, according to the following equation:—

$$C_6H_5CO.CH(C_2H_5).COOC_2H_5 + 2KOH = C_6H_5COOK + CH_2(C_2H_5).CO_2K + C_2H_5OH.$$

As in the case of substituted acetoacetic ethers, it was found on using very concentrated potash that mostly organic acids were formed, and that in order to get a good yield of phenylpropylketone, it is advisable to use the alkali, moderately dilute, and to digest for a longer time.

Diethylbenzoylacetic Acid.

From the foregoing it is clear that one of the hydrogen-atoms in the methylene-group in benzoylacetic ether may be replaced by alcohol radicals, the result being the production of homologues of this ether, exactly corresponding in the aromatic series to the substituted acetoacetic ethers in the fatty series. It remained, however, to be tested, whether the second hydrogen-atom could, in like manner, be replaced, *e.g.*, by ethyl, producing diethylbenzoylacetic ether. This, as a matter of fact, is the case. The experiment was carried out in the following way:—

A mixture of 1·2 gram of sodium (dissolved in about 20 c.c. of absolute alcohol), 10 grams benzoylacetic ether, and 10 grams ethyliodide, were heated in a sealed tube for about three hours to 100°.

At the end of this time, the product having become neutral, the alcohol was distilled off, then 1·2 gram of sodium (dissolved as before in 20 c.c. of absolute alcohol) added to the residue, and the whole was heated with 10 grams of ethyliodide three or four hours to 100°.

The reaction takes place in two phases. In the first place ethylbenzoylacetic ether is formed, which is then further acted on by the sodium ethylate and ethyliodide, forming diethylbenzoylacetic ether, according to the following equation :—

$$C_6H_5.CO.C(C_2H_5)Na.COOC_2H_5 + C_2H_5I = C_6H_5.CO.C(C_2H_5)_2.COOC_2H_5 + NaI.$$

At the end of the reaction the alcohol is distilled off, the residue diluted with water, and extracted several times with ether. After distilling off the ether the diethylbenzoylacetic ether remains behind as a thick dark brown oil, which, as it could not be purified by distillation, was directly saponified and the acid examined.

For this purpose the ether was dissolved in alcohol, and after adding very dilute alcoholic potash, allowed to stand for some weeks at ordinary temperatures. The product was then diluted with water, and any unsaponified diethylbenzoylacetic ether removed by extracting several times with ether. On acidulating the solution of the potash salt with dilute sulphuric acid, an oily acid was precipitated, which, on standing for some time and continually stirring, became quite solid. It was once or twice extracted with ether, and the ethereal solution dried over calcium chloride. On distilling off the ether, diethylbenzoylacetic acid remained behind as a brownish crystalline mass, which was spread on a porous plate to remove traces of oil. The acid, which was now only slightly yellowish coloured, was purified by dissolving in dilute ammonia and agitating with animal charcoal. On filtering and acidulating with dilute sulphuric acid, the acid was obtained in the form of an almost colourless crystalline solid. Although the saponification was conducted at ordinary temperatures, and with very dilute potash, the diethylbenzoylacetic acid always contained traces of benzoic acid, which spoilt the analytical numbers and melting point.

0·2121 gram substance gave 0·1325 gram H_2O and 0·5417 gram CO_2.

	Found.	Theory $C_6H_5.CO.C.(C_2H_5)_2.COOH$.
C =	69·66 per cent.	70·90 per cent.
H =	6·94 „	7·27 „
O =	23·40 „	21·81 „

The acid melts at 128—130°. Heated either alone or with dilute

sulphuric acid, it gives off carbonic anhydride, and an oil is left behind, probably diethylacetophenone.

Diethylbenzoylacetic acid is easily soluble in ammonia, soda, or sodic carbonate. On account of the difficulty of getting the acid pure, the salts were not further examined, it appearing probable that better results would be obtained on studying the decomposition-products of diethylbenzoylacetic ether.

Decomposition-products of Diethylbenzoylacetic Ether.

In order to examine these products, crude diethylbenzoylacetic ether was heated on a water-bath with dilute alcoholic potash for about five hours, by which means the ether was completely decomposed. After distilling off the alcohol and diluting with water, an oil was precipitated, which was separated from the solution of the potash salts by extracting with ether. The aqueous solutions were then gently warmed on a water-bath to get rid of the ether, acidulated with dilute sulphuric acid, and distilled in steam. A strongly acid slightly turbid distillate came over, which smelt strongly of the higher members of the acetic series, and probably contained diethylacetic acid. The residue on cooling deposited an acid, in the form of feathery crystals, which were collected on a filter and washed with water. The acid crystallised from water in silky plates, which possessed all the properties of benzoic acid. They melted at 120°, and gave the characteristic reaction with ferric chloride. In order to be certain, the acid was turned into the ammonia salt and precipitated with silver nitrate. An analysis of the silver salt gave the following numbers :—

0·2994 gram substance gave 0·1420 gram silver.

Found.	Theory C_6H_5COOAg.
Ag = 47·43 per cent.	47·16 per cent.

Diethylbenzoylacetic ether is therefore decomposed on heating with dilute alcoholic potash, partly into benzoic acid and diethylacetic acid, according to the equation :—

$$C_6H_5.CO.C(C_2H_5)_2.COOC_2H_5 + 2KOH = C_6H_5.COOK + CH(C_2H_5)_2.CO_2K + C_2H_5OH.$$

The neutral oils, produced by the action of potash on diethylbenzoylacetic ether which had been separated from the potash salts by extraction with ether, were next examined. After drying over calcium chloride and distilling off the ether, a dark brownish oil remained behind, which was fractioned. The principal portion which

distilled over between 220° and 235° gave, after several times carefully fractioning, an oil boiling constantly at 229—231° (at 710 mm.), which gave the following numbers on analysis, showing that diethylacetophenone had been formed:—

0·1711 gram substance gave 0·1371 H_2O and 0·5099 gram CO_2.

	Found.	Theory $C_6H_5.CO.CH(C_2H_5)_2$.
C =	81·28 per cent.	81·81 per cent.
H =	8·90 „	9·09 „
O =	9·82 „	9·09 „

Diethylacetophenone is a thick colourless oil, which does not solidify at 0°, the smell of which closely resembles that of acetophenone. Bromine acts easily on the solution in glacial acetic acid, on warming, quantities of hydrobromic acid being given off. The product is a colourless oil, which was not further examined, as it could not be purified by distillation, owing to decomposition, and on standing for some weeks over sulphuric acid *in vacuo*, it did not crystallise. The formation of diethylacetophenone by the action of potash on diethylbenzoylacetic ether may be expressed by the following equation:—

$$C_6H_5.CO.CH(C_2H_5)_2.COOC_2H_5 + 2KOH = C_6H_5.CO.CH(C_2H_5)_2 + K_2CO_3 + C_2H_5OH.$$

Allylbenzoylacetic Acid.

This acid and its decomposition-products were more especially examined, on account of their isomerism with benzoyltetramethylenecarbonic acid and benzoyltetramethylene obtained by the action of trimethylene bromide on benzoylacetic ether (an account of which I hope in a short time to be able to have the honour of laying before the Society), it being for several reasons interesting to determine any differences which might exist between these two bodies. Allylbenzoylacetic ether was prepared by the action of allyliodide on the sodium compound of benzoylacetic ether in the following way:—

10 grams of benzoylacetic ether were mixed with 1·2 gram of sodium (dissolved in about 15 c.c. of absolute alcohol), and the whole, after adding an excess of allyliodide heated on a water-bath for about four hours, or better still in a sealed tube to 100° for two hours, after which the mass had acquired a neutral reaction. The alcohol was then distilled off, the residue diluted with water, and several times extracted with ether. After drying over chloride of calcium and distilling off the ether, allylbenzoylacetic ether remained behind as a thick brownish oil, which, as it could not be distilled without decomposition, was not directly analysed.

In order to obtain allylbenzoylacetic acid, the crude ether was dissolved in alcohol, a little dilute alcoholic potash added, and the whole allowed to stand at ordinary temperatures for three weeks. The product was then diluted with water, and any unsaponified ether removed by extraction with ether.

The solution of the potash salts was then acidulated with dilute sulphuric acid, and once or twice extracted with ether. After distilling off the ether, the acid remained behind as a brownish crystalline mass, which was first roughly purified by spreading out on a porous plate.

In this manner the acid was obtained as a yellowish crystalline mass, which was very easily soluble in most of the ordinary solvents, and for this reason could not be satisfactorily recrystallised from any of them. It was therefore dissolved in dilute ammonia, and after shaking with animal charcoal and filtering, reprecipitated and analysed with the following result:—

0·1570 gram substance gave 0·0787 H_2O and 0·4005 CO_2.

	Found.	Calculated, $C_6H_5.CO.CH(CH_2.CH:CH_2).CO_2H$.
C =	69·57 per cent.	70·58 per cent.
H =	5·57 ,,	5·78 ,,
O =	24·86 ,,	23·53 ,,

The acid always seems to contain traces of benzoic acid, which spoil the analytical numbers and melting point. It melted at 122—125°, and on further heating either alone or with dilute sulphuric acid, gave off carbonic anhydride and an oil, probably allylacetophenone. I hope later on, if possible, to find some other more suitable means of saponifying diethyl- and allyl-benzoylacetic ethers, and of thus obtaining the acids in a purer state.

Decomposition-products of Allylbenzoylacetic Ether.

The best proof of the formation of allylbenzoylacetic ether in the foregoing experiments was the study of its decomposition-products. In order to examine these, 10 grams of crude allylbenzoylacetic ether were heated for two or three hours with dilute alcoholic potash on a water-bath, by which means it was completely decomposed. After distilling off the alcohol, the residue was diluted with water, and in order to remove the neutral oils from the solution of the potassium salts, it was several times extracted with ether. The ethereal solution, after drying over calcium chloride and distilling off the ether, deposited 5 grams of a dark-brown oil, which was then fractioned.

The principal quantity distilled over between 230° and 240°, and

gave on oft-repeated fractionation, an oil boiling constantly at 235—238° (at 710 mm. pressure), which on analysis gave numbers agreeing with those required for allylacetophenone.

0·1248 gram substance gave 0·0852 gram H_2O and 0·3757 CO_2.

	Found.	Theory, $C_6H_5.CO.CH_2.CH_2.CH:CH_2$.
C =	82·10 per cent.	82·50 per cent.
H =	7·58 „	7·50 „
O =	10·32 „	10·00 „

Allylacetophenone is formed by the action of alcoholic potash on allylbenzoylacetic ether according to the following equation:—

$$C_6H_5.CO.CH(CH_2.CH:CH_2).CO_2C_2H_5 + 2KOH = C_6H_5.CO.CH_2.CH_2.CH:CH_2 + K_2CO_3 + C_2H_5OH.$$

Allylacetophenone is a colourless oil, boiling without decomposition at 235—238° (710 mm.).

It has a curious smell, something like that of camphor, and a burning taste. It is insoluble in water, but dissolves in most of the other solvents. It does not appear to combine with acid sodium sulphite.

The potash salts, which were separated from the allylacetophenone by extraction with ether, were evaporated nearly to dryness on a water-bath, acidulated with dilute sulphuric acid, and distilled in steam. The distillate, which had a strong acid reaction, was filled with drops of an unpleasantly smelling oil, which dissolved easily in a solution of sodium carbonate, and consisted probably of allylacetic acid.

The residue in the retort, on cooling, deposited a quantity of colourless crystals, which were filtered off and recrystallised from water. They then melted at 118—120°, gave with ferric chloride a reddish-brown precipitate, and showed all the properties of benzoic acid. It is therefore probable that part of the allylbenzoylacetic ether had been saponified by the action of the alcoholic potash into allylacetic acid, benzoic acid, and alcohol, according to the following equation:—

$$C_6H_5.CO.CH(CH_2.CH:CH_2).CO_2C_2H_5 + 2KOH = C_6H_5CO_2K + CH_2:CH.CH_2.CH_2.CO_2K + C_2H_5OH.$$

Action of Bromine on Allylacetophenone.

Allylacetophenone being an unsaturated body, it appeared interesting to try the action of bromine on it, in the hope of obtaining a

crystalline addition-product. The experiment was carried out in the following way:—

Pure allylacetophenone was dissolved in glacial acetic acid, and after weighing the mixture, bromine slowly run in.

The colour of the bromine disappeared instantly at first; after a time, however, much more slowly, without the evolution of hydrobromic acid, the mixture becoming warm, rendering it necessary to cool the mass with water.

As soon as the colour of the bromine was permanent, the whole was re-weighed, when it was found that 1 mol. of allylacetophenone had taken up two atoms of bromine, according to the equation—

$$C_6H_5.CO.CH_2.CH_2.CH : CH_2 + Br_2 = C_6H_5.CO.CH_2.CH_2.CHBr.CH_2Br.$$

In order to isolate the product, the acid solution was poured into water, allylacetophenone dibromide being precipitated as a heavy oil, which was extracted with ether.

The ethereal solution was then washed once or twice with dilute sodic carbonate to remove any acetic acid, and finally dried over potassic carbonate. After distilling off the ether, a thick colourless oil remained behind, which, after standing over sulphuric acid *in vacuo* for 14 days, did not crystallise.

An analysis of this crude product gave the following numbers:—

0·3180 gram substance gave 0·3812 gram AgBr = 51·01 per cent. Br.
Theory for $C_6H_5.CO.CH_2.CH_2.CHBr.CH_2Br$ = 50·00 per cent.

If the solution of allylacetophenone dibromide in glacial acetic acid be further treated with bromine, at the same time warming the mixture on a water-bath, the colour of the mixture rapidly disappears, large quantities of hydrobromic acid being given off. In this experiment 4 grams of allylacetophenone dibromide, dissolved in glacial acetic acid, were treated with 1 gram of bromine, the whole being warmed on a water-bath till the reddish colour had disappeared.

On pouring the liquid into water, an oil was precipitated which was extracted with ether.

After washing the ethereal solution with sodium carbonate and distilling off the ether, a thick oil remained behind, which, on standing for some days over sulphuric acid in a vacuum, deposited a quantity of crystals. These were roughly separated from the oily products by spreading them out on a porous plate, and finally once or twice recrystallised from dilute alcohol.

The analysis gave the following result:—

0·4196 gram of substance gave 0·587 gram AgBr = 59·53 per cent. Br.
Theory for $C_{11}H_{11}OBr_2$ = 60·15 „

The substance was therefore bromallylacetophenone dibromide.

This body crystallises from dilute alcohol in four-sided prisms which melt at 121—122°.

It is easily soluble in alcohol, benzene, chloroform, ether, and carbon disulphide. In caustic soda, it dissolves with a yellow colour.

XXX.—*The Composition of Coal and Cannel Gas in Relation to their Illuminating Power.*

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Having had occasion during the past two or three years to investigate the composition of several kinds of illuminating gas, it has occurred to me that, as published analyses of coal-gas are by no means numerous, it might be interesting to examine in detail the nature of the gas supplied to some of the more important towns of the United Kingdom. I have been more especially induced to undertake this investigation in order to illustrate practically some of the results which I have recently arrived at in studying the laws to which the illuminating power of gas is subject.

In the year 1851, the metropolitan gases were examined by my father, and 25 years later, in 1876, by Dr. Humpidge, and the results of their analyses are recorded in the *Journal of the Chemical Society*, 1877, p. 624. As the analytical methods employed in their examinations were the same as those which I have also made use of, the three sets of results are interesting for comparison, and show the result of 33 years' experience on the manufacture of gas.

The constituents of the gas which have been individually determined, are:—The hydrocarbons absorbed by fuming sulphuric acid, carbonic anhydride, oxygen, nitrogen, hydrogen, carbonic oxide, and marsh-gas. In all cases, also, the carbon-density of the hydrocarbons has been determined, and in many cases also their hydrogen-density; the carbon and hydrogen densities together representing the average molecular formula of the hydrocarbons present.

The carbon-density is determined by exploding some of the gas with excess of oxygen, and then absorbing with caustic potash to ascertain the amount of carbonic anhydride formed. This total carbonic anhydride is then calculated for 100 vols. of gas, and then from this percentage is subtracted the sum of the CO_2, due to the com-

bustion of marsh-gas and carbonic oxide, together with any CO_2 that may be present as such in the gas; the residual CO_2 is then due only to the combustion of the hydrocarbons in 100 vols. of gas. If this percentage is divided by the percentage of hydrocarbons, the quotient is the carbon-density, whilst the percentage of residual carbonic anhydride, divided by 2, indicates the percentage of ethylene to which the hydrocarbons are equivalent, since 1 vol. of C_2H_4 produces 2 vols. of CO_2.

The hydrogen-density, on the other hand, is determined by ascertaining the total amount of oxygen required for the complete combustion of 100 vols. of gas, and then subtracting from that the oxygen required for the combustion of hydrogen, carbonic oxide, marsh-gas, and carbon of the hydrocarbons; the remaining oxygen is that required for the hydrogen of the hydrocarbons in 100 vols. of gas.

Now, since 1 vol. of oxygen combines with 2 vols. of hydrogen, and since the molecule of oxygen occupies 2 vols., therefore the molecule of oxygen corresponds to 4 atoms of hydrogen; consequently the volume of residual oxygen must be multiplied by 4, and the product divided by the percentage of heavy hydrocarbons, when the quotient will indicate the number of hydrogen-atoms in the molecule of average hydrocarbons.

The process may be expressed by means of the following formula:—

$$\frac{A \times 4}{C} = \text{hydrogen-density.}$$

A = volume of oxygen consumed by hydrogen of hydrocarbons in 100 vols. of gas.

C = volume of hydrocarbons in 100 vols. of gas.

The reputed illuminating power is also recorded for each gas; also the ratio of the illuminating power to the proportion of ethylene to which the heavy hydrocarbons are equivalent.

On turning attention, in the first place, to the illuminating constituents of the gases, it will be seen from the average formulæ of the hydrocarbons, that the C_nH_{2n} or olefine series composes by far the greater part of the hydrocarbons; and since the carbon-density is almost invariably less than 3, the first and second terms of that series, or ethylene and propylene, must be the predominant hydrocarbons. That ethylene by itself, however, would be quite incapable of yielding the illuminating power indicated, is demonstrated, not only by my experiments with mixtures of ethylene and the several diluents of coal-gas, but also by actually adding ethylene to coal-gas disilluminated by bromine. Thus, I find that no less than 13 per cent. of ethylene must be added to the disilluminated gas of the Gaslight and Coke

Company, in order that it shall yield a light of 16 candles, whilst the same illuminating power is attained by the hydrocarbons actually present in the gas, although equivalent to only 6·58 per cent. of ethylene. Similarly, to make this gas produce a light of 28 candles, it is necessary to add no less than 31 per cent. of ethylene, whilst the St. Andrew's gas of 27 candles contains only the equivalent of 13·71 per cent. of ethylene. This clearly indicates how much of the actual illuminating power of gas is due to denser hydrocarbons, although they are present only in comparatively insignificant proportions.

Thus, I also find that if the disilluminated gas of the Gaslight and Coke Company be saturated with the vapour of benzene, 3 per cent. of benzene vapour, equivalent to 9 per cent. of ethylene, already imparts to the gas an illuminating power of about 23 candles, a light which is greatly in excess of that yielded when 13 per cent. of ethylene itself is added to the disilluminated gas. These determinations are recorded in the following table:—

Percentage composition of gas.		Observed illuminating power in standard candles.	Rate.		Candle-power calculated to 5 cubic feet of gas, and 120 grains of spermaceti.
			Cubic feet of gas consumed per hour.	Grains of spermaceti consumed per hour.	
Disilluminated gas.	C_2H_4.				
86·59	13·41	18·68	5·60	116·2	16·84
68·98	31·02	24·94	4·32	118·1	28·40
Disilluminated gas.	C_6H_6.				
96·91	3·09*	13·06	2·60‡	109·3	22·92
96·70	3·30†	10·20	2·11‡	120·0	24·17

Taking the gases in groups, the members of each group having the same illuminating power, it will be seen that the same light is produced by hydrocarbons which are equivalent to considerably different proportions of ethylene. Thus:—

* Temperature of benzoliser 15·5° C.

† Temperature of benzoliser 17·0° C.

‡ Cubic feet of disilluminated gas consumed per hour, the benzoliser being placed between the meter and the burner.

Illuminating power in standard candles.	C_nH_m per cent. maximum and minimum.	Equivalent to C_2H_4, maximum and minimum.	Value of 1 per cent. of C_2H_4 in standard candles.
30 (?)	12·23	16·55	1·81
27	10·04—10·00	13·40—13·71	1·97—2·01
21·5	7·90	9·50	2·26
20	6·22	8·41	2·38
18·5	5·63	8·24	2·25
18	7·28— 6·28	10·64— 8·78	1·69—2·05
17·25	4·76	6·28	2·75
17	4·58	7·77	2·19
16	4·95— 2·92	7·10— 4·42	2·25—3·62
15	4·53	5·67	2·65
14	4·53— 3·09	5·82— 4·60	2·40—3·04
			Average (cannel) 2·02
			„ (coal) 2·71

A glance at this table shows that the gases of high illuminating power, and these are all cannel-gases, have a considerably lower candle value for each per cent. of ethylene-equivalent than the coal-gases of lower illuminating power. From the average formulæ of the hydrocarbons in these cannel-gases it will be seen that they belong almost exclusively to the C_nH_{2n} or olefine series, whilst the coal-gases contain larger proportions of hydrocarbons belonging to the more condensed series.

On comparing the analyses of coal-gas made in 1851 with those in 1876 and 1883, it will be seen that some changes have taken place. In the first place the carbon-density has undergone progressive diminution, being greater in 1851 than in 1876, greater in 1876 than in 1883. The high carbon-density of the cannel coal in 1876 is especially noticeable, being considerably greater than that of any of the coal-gases.

The samples of gas analysed in 1851 appear to have been practically free from nitrogen, other than that present as atmospheric air, whilst some of the samples analysed in 1876, and by myself, contain a very considerable percentage of nitrogen, over and above that present as atmospheric air. This excess of nitrogen in the later analyses must necessarily have been derived from the atmosphere, and become deprived of its oxygen in the process of manufacture. For taking the percentage of nitrogen in coal as 2, which is certainly considerably above the truth, it appears, from a paper recently read by Mr. Foster before the Institute of Civil Engineers, that from 21 to 36 per cent. of the nitrogen present in the coal is unaccounted for, either in the residual coke or in the nitrogenous compounds formed on distillation. Now 21—36 per cent. of the nitrogen in coal corresponds to 127—

Town.	Reputed illuminating power in standard candles.	Composition of coal and cannel gases, 1882–4.										Ratio :— Illuminating-power / Equivalent of C_2H_4 per cent. or Equivalence of 1 per cent. C_2H_4 in standard candles.	Coal used.
		Hydrocarbons, C_nH_m.	Equivalent of C_nH_m in C_2H_4.	Average formula of C_nH_m. C.	Average formula of C_nH_m. H.	CO_2.	O.	N.	H.	CO.	CH_4.		
Edinburgh	(30?)	12·23	16·55	2·71	5·38	0·35	1·00	3·64	33·24	6·61	42·93	1·81	Cannel.
Glasgow	27	10·00	13·40	2·68	5·09	0·29	0·06	3·07	39·18	7·14	40·26	2·01	,,
St. Andrews	27	10·04	13·71	2·73	—	2·73	0·48	2·83	36·63	5·16	42·13	1·97	,,
Liverpool	21·5	7·90	9·50	2·41	—	1·70	0·19	6·10	36·44	3·39	44·28	2·26	,,
Preston	20	6·22	8·41	2·70	—	0·84	0·25	4·79	43·95	4·62	39·33	2·38	,,
Nottingham	18·5	5·63	8·24	2·93	—	0·81	0·24	2·51	45·52	5·63	39·66	2·25	Coal.
Leeds	18	7·28	10·64	2·92	—	0·34	0·07	4·32	40·23	5·02	42·74	1·69	Cannel.
Sheffield	18	6·28	8·78	2·79	—	0·24	0·10	2·56	43·05	4·72	43·05	2·05	,,
Birmingham	17·25	4·76	6·28	2·64	4·29	1·50	0·36	10·10	40·23	4·05	39·00	2·75	Coal.
Bristol	17	4·58	7·77	3·39	—	none	0·27	5·11	44·57	4·77	40·70	2·19	,,
London	—	—	—	—	—	—	—	—	—	—	—	—	
Gas Light and Coke Co.	16	4·41	6·58	2·98	4·32	none	0·26	5·95	47·99	3·75	37·64	2·43	,,
South Metropolitan	16	2·92	4·42	3·03	5·16	0·09	none	3·19	53·14	4·11	36·55	3·62	,,
Redhill	16	4·40	5·91	2·69	4·58	0·74	0·49	3·37	48·18	3·41	39·41	2·71	,,
Gloucester	(16?)	4·95	7·10	2·87	—	0·03	0·51	2·73	48·89	4·64	38·25	2·25	,,
Newcastle-on-Tyne	16	3·62	5·00	2·76	—	0·28	0·23	5·29	50·50	3·37	36·71	3·20	,,
Newcastle, Staffordshire.	15	4·53	5·67	2·47	—	0·08	0·11	6·22	46·31	3·74	39·01	2·65	,,
Brighton	14	3·76	4·60	2·45	4·62	0·03	0·23	2·07	51·62	4·14	38·15	3·04	,,
Southampton	14	3·09	4·90	3·17	5·20	0·07	0·39	2·53	53·59	3·59	36·74	2·86	,,
Ipswich	14	4·53	5·82	2·57	3·77	0·06	0·12	10·84	43·26	2·46	38·73	2·40	,,
Norwich	(14?)	3·26	4·85	2·97	3·40	0·27	0·14	3·03	53·79	3·40	36·11	2·89	,,

217 cubic feet of nitrogen from 1 ton of coal, and taking the gas produced from 1 ton of coal as 10,000 cubic feet, the nitrogen in the coal-gas would amount to from 1·27 to 2·17 per cent. by volume. To this must be added the nitrogen which is occluded in the coal, which from the researches of Mayer (*J. pr. Chem.*, 1872, **113**, 407) averages, in the English coal examined by him, 48 per cent. of the total occluded gases. The mean volume of occluded gases amounts to 25 cubic inches in 1 lb. of coal, or 32 cubic feet in 1 ton, so that the nitrogen from this source would be 15 cubic feet per ton, or, taking 10,000 cubic feet as the total yield of gas per ton of coal carbonised, 0·15 per cent. of nitrogen by volume in the coal-gas, an amount which is, therefore, quite insignificant. There can be no doubt that the larger quantities of nitrogen found in the later analyses of coal-gas, are due to the replacement of the iron retorts, which were almost exclusively used before, by the porous fire-clay retorts, which are also more liable to fissure, together with the increased exhaustion of the retorts during distillation. A certain amount of atmospheric air or furnace gas is thus sucked in, deprived of its oxygen in the retort; the carbonic anhydride formed is of course removed in the process of purification, and the nitrogen only remains in the final product. Moreover, the same result would be attained if air were aspirated into the gas at any other point before passing through the purifiers, since in the latter it would be deprived of its oxygen by the reducing action of the calcium and iron sulphides, the nitrogen alone remaining in the purified gas.

XXXI.—*On the Reaction between Hydrogen Chloride and Selenium Sulphoxide.*

By Edward Divers and Masachika Shimosé.

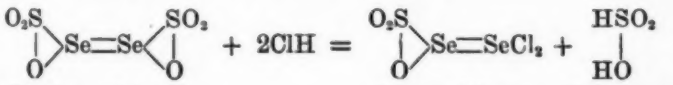
Selenium dissolves sparingly in sulphuric acid, imparting to it, as is well known, a green colour, and existing in it almost certainly as selenium sulphoxide, $SeSO_3$. This solution reacts with gaseous hydrogen chloride, evolving sulphur dioxide and changing in colour; but the reaction is soon impeded by the presence of water as one of its products. When fuming sulphuric acid is used in place of the ordinary acid, the reaction proceeds without check, and, besides this, the selenium dissolves freely in the fuming acid.

As the hydrochloric acid passes, the solution slowly becomes deep brown-red and turbid, deposits drops of a deep red heavy liquid, and

gradually lightens in colour again until yellow-brown. Much of the hydrochloric acid escapes absorption, and carries with it a little vapour of the red liquid, and, at first, considerable quantities of sulphur dioxide.

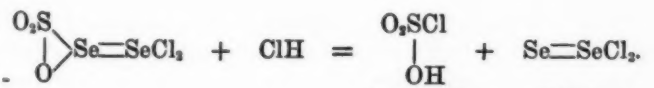
The heavy red liquid is selenium selenochloride, Se_2Cl_2. Its light yellow-brown fuming mother-liquor reacts of course violently with water, and deposits at the same time some selenium. But the mother-liquor also reacts violently with ordinary sulphuric acid, evolving torrents of hydrochloric acid. The source of this hydrochloric acid is assuredly sulphuryl hydroxychloride; for according to Dewar and Cranston (*Chem. News*, **20**; *Watts's Dict.*, **6**, 1069), sulphur trioxide dissolved in *sufficient quantity* in sulphuric acid forms the hydroxychloride with hydrochloric acid; while according to S. Williams (*Chem. Soc. J.*, **22**, 306), on the other hand, the hydroxychloride is decomposed by sulphuric acid in *great excess*.*

The reaction of the sulphuric acid solution of selenium sulphoxide with hydrochloric acid, consisting as it does, first, in the conversion of the green sulphoxide-coloured solution into the red selenochloride-coloured one, and, secondly, in the remarkable precipitation of the selenochloride and simultaneous formation of sulphuryl hydroxychloride, has suggested to us the following theory, which appears to be closely in accordance with facts. Doubling the formula of selenium sulphoxide, the two equations run thus:—



Selenium sulphoxide. Selen. sulphoxychloride. Sulphurous (sulphonic) acid.

and



Sulphuryl hydroxychloride. Selenium selenochloride.

Selenium selenochloride is insoluble in ordinary sulphuric acid and quite unaffected by it, but is freely dissolved by the fuming acid, forming a green solution. No noticeable heating occurs, and no evolution of either sulphur dioxide or hydrochloric acid. This solu-

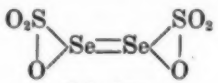
* Beckurts and Otto (*Ber.*, 11, 2058) express doubts as to the accuracy of Williams's observation, but our own observations, recorded in this paper, go far to substantiate it. We would suggest that the stability of sulphuryl hydroxychloride, in presence of sulphuric acid, is not so much dependent upon *mass*, as these chemists surmise, as upon *temperature*,—that is, in the cold, sulphuric acid decomposes the hydroxychloride; in the heat, hydrochloric acid decomposes pyrosulphuric acid.

tion changes colour with hydrochloric acid, gives a precipitate of the red selenochloride, and does so much faster than a solution of selenium itself in fuming sulphuric acid.

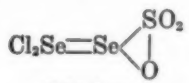
This behaviour of selenium selenochloride agrees perfectly with the above theory. The not yet isolated *selenium sulphoxychloride* is represented as having a constitution closely related to that of selenium sulphoxide, and its decomposition by hydrochloric acid and the precipitation of selenium selenochloride from want of sulphur trioxide to combine with, follow naturally from the theory.

It seems certain, if more sulphur trioxide is present than is needed to make selenium sulphoxide, that the hydrochloric acid will react with the excess of trioxide to form hydroxychloride, after it has converted all the selenium sulphoxide into sulphoxychloride, and before it proceeds to decompose this body into a further quantity of hydroxychloride and selenium selenochloride.

Selenium and its selenochloride have in their behaviour three special points in common. They are scarcely soluble in ordinary sulphuric acid; they are freely soluble in fuming sulphuric acid; and their solutions have the same green colour. A reason for this is formed by attributing to the compounds having the green colour an analogous constitution, expressed by the formulæ



Selenium sulphoxide.



Selenium sulphoxychloride.

which lead further to that of $Se{=}SeCl_2$ (selenium selenochloride), for the chloride, analogous to $SSCl_2$ (sulphur thiochloride), proposed by Michaelis and Schifferdecker (*Ber.*, **5**, 924), for the sulphur compound, and supported by Thorpe's investigations (*Chem. Soc. J.*, **37**, 389). As, now, according to this view, the union of selenium selenochloride with sulphur trioxide is attributed to a latent combining power of the atom of selenium acting as a diad, we should expect that sulphur thiochloride would also combine with sulphur trioxide, and that sulphur monoxychloride would not. This seems to be the case from the literature of the subject, although a definite compound of sulphur thiochloride has not been described; for the liquid obtained by Rose can hardly be regarded as such.

The reaction which is the subject of this paper, is very interesting in affording an example of a new aqua regia, in which pyrosulphuric acid functions as nitric acid:

$$H_2S_2O_7 + 4HCl = 2SO_2 + 2Cl_2 + 3H_2O.$$

We have ourselves no claim to the discovery of this elegant method

of forming certain chlorides from their simple substances, as in 1882 Heumann and Köchlin pointed out (*Ber.*, **15**, 420) that tin and fuming sulphuric acid yield tin tetrachloride with hydrochloric acid. They also showed that the action of sulphur on sulphuryl hydroxychloride gives rise to sulphur thiochloride. Our own experiments were made, however, in ignorance of the work of these chemists.

Reaction between Sulphur Trioxide and Selenium Selenochloride.

We have made some experiments upon the reaction between sulphur trioxide and selenium selenochloride in the absence both of sulphuric and hydrochloric acids. As, however, the results of these experiments appear to be at variance with those of H. Rose and with those of Clausnizer (*Ber.*, **11**, 2008), they need our careful verification before they are offered as trustworthy, and this we have no opportunity of giving them at present, though we hope to be able to resume this work in a few months.

For the present we limit ourselves to stating that by this reaction an unstable green liquid is first obtained without any evolution of sulphur dioxide, and that then a transformation of this proceeds, in which a bright-yellow crystalline solid is formed, together with other substances, with consumption of more sulphur trioxide, and production of sulphur dioxide in some quantity.

The green matter is apparently the selenium sulphoxychloride, $Cl_2Se_2SO_3$, the existence of which has been assumed in the present paper, but it may possibly be green sulphoxide in some kind of solution. We reserve details for our future publication, though we do not see that any fuller examination of this unstable matter will be possible.

The products of transformation of the green liquid and sulphur trioxide appear from our analyses to include yellow selenium sulphoxide or a compound of this, sulphuryl oxychloride, $S_2O_5Cl_2$, and the analogue of this, sulphoselenium oxychloride, $SSeO_5Cl_2$. But here we must be wrong if those preceding us in the work are right: for according to them, selenium tetrachloride and sulphur trioxide unite to form a compound, SO_3SeCl_4, analogous to the sulphur oxytetrachloride of Millon, $S_2O_3Cl_4$, but unlike it in being quite stable, and therefore not yielding $S_2O_5Cl_2$, and, above all, not any selenium compound in which the selenium can be a hexad, such as $SSeO_5Cl_2$ would be. We find difficulties in the way whether we accept our own conclusions or reject them, and are therefore eagerly awaiting the time when we may be able to clear up the matter.

XXXII.—*Selenium Selenochloride.*

By Edward Divers and Masachika Shimosé.

By the reaction between hydrochloric acid and a solution of selenium in fuming sulphuric acid, selenium selenochloride can now, for the first time, be obtained pure. That it could be prepared from the above reagents might have been foreseen from the recent observations of Heumann and Köchlin on the formation of tin tetrachloride in a similar way, and of sulphur thiochloride from sulphuryl hydroxychloride and sulphur.

Berzelius prepared selenium selenochloride by heating selenium with its tetrachloride, and Sacc by treating fused selenium with chlorine, and collecting what volatilised. (*Watts's Dict.*, **6**.) As was to be expected, analyses of such preparations did not give results agreeing with theory (*Jahrb. f. Min.*, **1**): for this chloride cannot be distilled without decomposition, and, as it is decomposed by heat, cannot by this agent be freed from tetrachloride in a definite manner. The descriptions given of it show that, as thus obtained, it was far from pure.

The passage of hydrochloric acid gas through fuming sulphuric acid solution of selenium gradually precipitates selenium selenochloride. After preparation in this way it is purified, more especially from an excess of selenium, by replacing its mother-liquor with fresh fuming sulphuric acid, in which it readily dissolves. The solution is then submitted to a stream of hydrochloric acid, which rapidly reprecipitates the chloride. (See the paper preceding this.) Separated from its second mother-liquor, it becomes pure after digestion with dry potassium chloride (with exclusion of moist air as a matter of course), in order to remove traces of sulphuric acid. Decanted from this, it is pure.

It is a heavy liquid with a fine deep red colour—not brown as hitherto described. It has an odour resembling that of sulphur thiochloride, but not so strong, and becoming pungent only with the formation of hydrochloric acid by the moisture of the air. It has the property, shown by a few other liquids, of not actually touching a surface of glass against which it rests, unless this is exceptionally clean.

The Sprengel-tube for taking its specific gravity had therefore to be slightly modified. The usually horizontal extremities of the tube were, for this purpose, inclined a little upwards, and for adjusting the liquid the tube so fixed that the mouth of the capillary limb was level

with the mark on the other limb. The adjustment of the liquid having been made, the tube was restored to the vertical for weighing.

Using 6·924 grams, and with the temperature of the air 17·5°, the specific gravity has been found to be 2·906.

It is slightly volatile at common temperatures, and in warm weather sublimes slowly in a sealed tube. At the temperature of a water-bath, a thin orange-coloured vapour is given off, which condenses to drops having a red colour, showing that some of the liquid distils unchanged. But the heating causes dissociation, the higher chloride volatilising and selenium accumulating in the unvolatilised liquid.

Chloroform freely dissolves selenium selenochloride, but in a very peculiar way. As the two liquids mix, a copious red precipitate of selenium appears, but at once redissolves on shaking. Each further addition of selenium chloride is followed by fresh precipitation and redissolution. The solution has the colour of the selenium selenochloride, and the chloroform can be readily boiled away, so as to leave the selenium chloride behind. Then, if to this residue of selenium selenochloride fresh chloroform is added, the same phenomena recur. Previous long digestion of the chloroform with sulphuric acid, to ensure absence of moisture, in no way affects the phenomena.

Anhydrous *benzene* behaves like chloroform, but only to a very slight degree. It freely dissolves selenium selenochloride. *Carbon tetrachloride* causes no precipitation of selenium. Both this and *carbon bisulphide* dissolve large quantities of the chloride. We have found no explanation for the remarkable momentary dissociation of selenium selenochloride, in which no doubt the tetrachloride forms, which happens with chloroform, and yet not with carbon tetrachloride.

Water (as also *alcohol* and *ether*) decomposes selenium selenochloride, but only slowly, leaving for some time a viscid mass of selenium and its chloride. *Potassium hydroxide* solution acts in almost the same slow and imperfect way. But by dissolving the selenochloride in carbon bisulphide, and shaking the solution with water, complete decomposition is readily effected, the selenium not dissolved as oxide being left in the pulverulent form.

Sulphuric acid scarcely dissolves it, and exerts no action upon it, although *fuming sulphuric acid* easily dissolves it, as already stated. (Its reaction with *sulphur trioxide* we describe in a future paper.) *Sulphur* dissolves to only a limited extent, and very slowly, in the selenochloride. *Mercury* and *silver* both decompose it, the latter becoming stained black.

Selenium selenochloride must be looked upon as constituted like sulphur thiochloride, and we have presented independent evidence of this in our paper on the reaction between selenium sulphoxide and hydrochloric acid.

We have still to state the methods and results of our analyses. The estimation of the selenium was a simple matter. Oxidation with nitric acid, heating with hydrochloric acid, precipitation by sulphur dioxide, filtering, drying, and weighing on a tared filter, completed this part of the work.

The estimation of the chlorine presented some difficulty. Acid oxidation would have entailed loss of chlorine, and decomposition by even concentrated solution of potassium hydroxide was very hard to accomplish. Decomposition by water alone was likewise very incomplete. However, by dissolving the chloride in carbon bisulphide, and shaking the solution with water, it was easily and completely decomposed. The carbon bisulphide and finely divided insoluble selenium were filtered off, and the filtrate mixed with a little nitric acid and titrated with silver nitrate solution—the acid being necessary to keep selenious acid from precipitating silver. The carbon bisulphide and precipitated selenium retained no trace of chlorine.

Of one preparation, 0·6522 gram was used for the selenium determination, and 0·6983 gram for the chlorine, fifths of the resulting solution being titrated. Of another preparation, 0·5820 gram was taken for the selenium, and 0·8467 gram for the chlorine. The results were: Se being taken as 79, and Cl as 35·4:—

	I.	II.	Theory.
Selenium	68·66	69·07	69·06
Chlorine	31·13	30·92	30·94
	99·79	99·99	100·00

The work described in this paper was completed six months ago, and the paper itself has been ready in our hands a considerable time. But circumstances have caused delay in sending it to the Society. Now, we have lately seen in the *Chemical News*, the briefest note of a paper by Messrs. Evans and Ramsay, read to the Society, on the halogen-compounds of selenium, which paper will no doubt have deprived ours of most of its novelty. We venture, however, still to offer it to the Society, as it may serve to confirm their results, if not to add to them.

XXXIII.—*On Selenium Sulphoxide.*

By Edward Divers, M.D., and Masachika Shimosé, Imperial Japanese College of Engineering, Tokio.

In our paper on tellurium sulphoxide, published by the Society last year, we showed that this substance, $TeSO_3$, first obtained by Rudolph Weber, exists in two modifications, a red and a brown. We now give the results of an examination of selenium sulphoxide undertaken to determine whether this also does not exist under two forms, as it then appeared to us to do.

Selenium sulphoxide has been described by Weber (*Pogg. Ann.*, **156**, 531). On bringing liquid sulphur trioxide in contact with powdered selenium, union occurs with rise of temperature. The selenium changes, directly it is moistened with the trioxide, into a very thick dark green liquid, transparent in thin layers, while the excess of sulphur trioxide remains quite colourless and unaltered. In about 10 minutes the green liquid solidifies to a crystalline mass, which does not resume the liquid state when heated. We prepared it for analysis in precisely the same way as we prepared tellurium sulphoxide.

The analysis we have made of the green sulphoxide agrees with Weber's formula, $SeSO_3$:—

Selenium taken	0·3582
Sulphur trioxide found	0·3588
Sum	0·7170
Selenium sulphoxide found.....	0·7165
Difference.....	−0·0005

Calculated to percentages, we get—

	Obtained.	Theory.
Selenium	49·99	49·69
Sulphur trioxide ..	50·07	50·31

Very slowly green selenium sulphoxide undergoes change at ordinary temperatures, shown by its becoming discoloured. It may, however, be heated to 35° for some time without appreciable alteration. That at least has proved to be the case with us in several instances, whilst Weber remarks that it is not decomposed by gentle heating. But in one case it happened to us that decomposition set up at the ordinary summer temperature, before even the excess of sulphur trioxide had been removed. We can suggest no explanation of this

difference of behaviour, but may point out that it is in accordance with what has been observed by Weber and ourselves in tellurium sulphoxide.

On heating selenium sulphoxide, decomposition begins to show itself at 40° by a change of the green colour to brown, and by the escape of sulphur dioxide, although this is exceedingly slow, even when 90° is reached. At 120° and upwards, however, sulphur dioxide is steadily evolved, the colour gradually changes to bright yellow, and the volume slightly shrinks. In that instance in which sulphur dioxide escaped freely at common temperatures, very little came off afterwards on heating the mass until it had turned yellow.

On continuing the heat the colour changes to orange, and then reddens and darkens until it becomes identical with that of selenium. Selenium, in fact, is here formed together with its ordinary oxide. Attempts to get the oxide corresponding to the tellurium monoxide, we have elsewhere described, failed.

By heating slowly and maintaining a moderate temperature for a long time, the sulphoxide changes, *in vacuo*, almost perfectly to a yellow amorphous mass. With more rapid heating, reddening occurs before the yellowing stage is completed, and the mass contains a much greater proportion of selenium than when the heat is better graduated.

We have analysed four preparations of the yellow mass, in the way we have described in our tellurium sulphoxide paper. They were heated more and more gradually, in the order in which they were prepared and now are numbered. The last one is that in which decomposition was active at common temperatures:—

	I.	II.	III.	IV.
Selenium	0·5318	0·6210	0·6700	0·3764
Sulphur trioxide	0·2612	0·3295	0·4137	0·3003
Sum	0·7930	0·9505	1·0837	0·6767
Selenium sulphoxide	0·8256	0·9885	1·1300	0·7040
Difference.....	0·0326	0·0380	0·0463	0·0273

These results do not agree among themselves, and, moreover, all of them show an excess of oxygen, appearing as the difference between the weight of the product and the sum of the selenium and sulphur trioxide contained in each. Nevertheless, we consider as almost certain that these preparations were mixtures of a yellow selenium sulphoxide with selenium and its dioxide, for reasons we proceed to state.

The yellow mass hisses when thrown into water, just like the green sulphoxide and the tellurium sulphoxides, and is therefore a sulphuric oxide compound; it bears a heat of 120°, and therefore its sulphur trioxide is in combination; it does not contain any green sulphoxide, by which its properties might be explained; and its yellow colour cannot be regarded as due to free selenium. According to Weber, when the green sulphoxide is crushed, the powder is yellow. Further, on calculating to percentages, on the assumption that the preparations analysed were mixtures of the sulphoxide with selenious oxide and selenium, and arranging the results, these suggest, by their relations, the probable correctness of the assumption. Lastly, by the action of selenium selenochloride upon sulphur trioxide, there is produced, as we shall describe in a future paper, a bright yellow substance, which is apparently also selenium sulphoxide.

We now give the calculated percentages :—

	I.	II.	III.	IV.
Selenium sulphoxide	62·8	66·3	72·8	84·8
Selenium dioxide.....	13·9	13·5	14·3	13·3
Selenium in excess	23·3	20·3	12·9	2·0

in which there are several things to attract notice. The more gradually the preparations had been heated, the more sulphoxide they contained, and, in the same order, the less free selenium they contained, while, throughout, the selenium dioxide was practically constant.

In the fourth preparation much of the selenium dioxide must have been produced from extraneous sulphur trioxide, since from selenium sulphoxide alone there would be as much selenium set free as that contained in the dioxide produced :—

$$2SeSO_3 = Se + SeO_2 + 2SO_2.$$

Now it was in this fourth experiment that sulphur dioxide was freely evolved before the excess of trioxide had been evaporated. In the other preparations, particularly the first and second, the free selenium is in greater quantity than is equivalent to the selenium dioxide.

The cause of the selenium dioxide being present in nearly constant proportions, is not very evident, and in the form in which we have cast our results, this constancy may appear a chance coincidence. But by referring the oxygen to a constant quantity of selenium, it still comes out nearly constant :—

	I.	II.	III.	IV.
Selenium	100	100	100	100
Sulphur trioxide	49	53	62	79
Oxygen	6	6	7	7

The great excess of free selenium in the first two preparations proves that selenium sulphoxide must decompose, at least in part, to selenium and sulphur trioxide again. We are therefore led to adopt the view that selenium sulphoxide does not decompose at once, thus:—

$$2SeSO_3 = Se + SeO_2 + 2SO_2,$$

but exclusively into selenium and sulphur trioxide, and that then some of the trioxide acts upon undecomposed selenium sulphoxide to produce the two dioxides, thus:—

$$SeSO_3 + SO_3 = SeO_2 + 2SO_2,$$

just as excess of trioxide must have acted in Experiment IV. With quick elevation of temperature much of the sulphur trioxide escapes, but with a gradual rise, only a little of it. Thus, in the third experiment, in which the free selenium and selenium dioxide are not far from equal in atomic proportion, only a little trioxide appears to have escaped without previous reduction.

With the sulphoxide of the more basic tellurium the reduction of the sulphur trioxide, when the sulphoxide is heated, is complete, a special oxide of tellurium being formed from the first. But it is probable that the fact we have pointed out in our paper on the tellurium compound, and could not then explain, respecting its decomposition by water, namely, that much more than half of the tellurium takes on the free state, is explicable as being the result of some of the tellurium sulphoxide reacting with water to form free tellurium and sulphuric acid.

Summary.—(1.) A yellow modification of selenium sulphoxide appears to exist, but has not been obtained pure. (2.) Selenium sulphoxide is resolved by heat into selenium and sulphur trioxide. (3.) Sulphur trioxide can oxidise selenium sulphoxide, producing selenium dioxide and sulphur dioxide. (4.) Tellurium sulphoxide, when decomposed by water, gives tellurium and sulphuric acid, and part of these then react to form sulphurous acid and tellurous acid.

XXXIV.—*Trichloropyrogallol.*

By Charles S. S. Webster.

The researches of Stenhouse and of Stenhouse and Groves (*Chem. Soc. J.*, **28**, 1 and 704) upon the action of chlorine and bromine upon the trihydric phenols and their derivatives, have remained for some years undeveloped. In the course of the investigations of Messrs. Cross and Bevan, with a portion of which I have been connected, it was found that by the action of chlorine in presence of water, upon lignose and bastose, chlorinated derivatives were obtained similar in properties and in composition to the derivatives obtained by the action of this element upon several of the astringent substances of natural origin. The most noticeable feature of this result was that while the latter are made up for the most part of compounds which are aromatic in the strict sense of the word, the former do not contain any compounds of this order, but are converted into such by the action of the chlorine. Lastly, it was found that the amorphous chlorinated derivative, $n(C_{19}H_{18}Cl_4O_9)$, obtained from bastose (jute), giving with sodium sulphite solution a characteristic colour reaction (magenta), had certain features of resemblance to the mairogallol, $C_{18}H_7Cl_{11}O_{10}$, obtained from pyrogallol by the authors above mentioned, sufficiently so to suggest a reinvestigation of the subject with the view of elucidating the mode of formation of this peculiar derivative.

In first preparing mairogallol according to the method of Stenhouse and Groves, it was noticeable that the reaction took place in two stages, as had in fact been observed by them; but they did not ascribe to the first its full significance. I find that it consists in the formation of a trichloropyrogallol, and it is therefore this compound which undergoes subsequent condensation, by the continued action of the chlorine in presence of the hydrochloric acid formed in the reaction, on the C_{18} derivative in question.

Since I can find no mention of a compound of this formula, $C_6Cl_3(OH)_3$, I will describe in detail the process by which it may be most conveniently prepared:—

To 5 grams pyrogallol in a large test-tube, 12·5 c.c. of strong acetic acid (60 per cent.) are added, a quantity insufficient for its solution. The test-tube is kept cool by being surrounded with water, and a rapid current of dry chlorine is passed through the liquid. Volumes of hydrochloric acid are then evolved, the colour changes to a deep reddish-brown, and in about half an hour the liquid, which is saturated with chlorine, coagulates to a semi-solid mass of fine needles of

the new compound. These are well drained from the mother-liquor, washed with acetic acid of sp. gr. 1·04, in which they are only slightly soluble, and recrystallised with the usual precautions, from one of its several solvents.

The following preparations were analysed:—

(*a*.) Prepared as above, recrystallised four times from alcohol and finally from benzene. (*b*.) Recrystallised five times from alcohol, and finally from benzene.

(*a*.) 0·2320 gave 0·3379 AgCl + 0·0055 Ag.
(*b*.) 0·2430 „ 0·3527 „ + 0·0102 „

	(*a*.)	(*b*.)	$C_6Cl_3(OH)_3.3H_2O$.
Per cent. Cl	36·7	37·2	37·5

This compound, which crystallises in fine needles, was found to exhibit reactions identical with those of tribromopyrogallol, notably that of giving a deep pure blue coloration with *the alkaline earths*. Heated at 115° between watch-glasses, the compound fused to a brown mass, giving also a slight sublimate, which was found to have the same reactions as the original; the loss of weight was estimated at 20 per cent (0·1900 lost 0·0380 = 20 per cent.), whereas $C_6Cl_3(OH)_3.3H_2O$, contains 19 per cent. H_2O; the brown residue was analysed and found to contain 44·7 per cent. Cl, the anhydrous compound containing 46·4, showing therefore that slight decomposition had taken place with loss of HCl.

A weighed quantity of the compound was then placed in a finely powdered state over sulphuric acid in a vacuum, and left for six days at the ordinary temperature; 0·2064 lost 0·0262 = 12·7 per cent. There was no further loss on again exposing for 24 hours.

The compound therefore loses $2H_2O$ under these conditions (calc. 12·7 per cent.); the resulting monohydrate loses its water on heating, but with difficulty. A portion was analysed after heating for 30 minutes at 110°:—

0·2896 gave 0·4984 AgCl + 0·0242 Ag.
0·1878 „ 0·2086 CO_2 and 0·0337 H_2O.

		Calc. $C_6Cl_3(OH)_3$.
C	30·30	31·3
H	1·97	1·3
Cl	45·30	46·4

The compound still retained, therefore, about 2 per cent. H_2O.

On further heating, it ultimately melts with decomposition at 177° (uncorr.).

This trichloropyrogallol has the following properties:—

It is only slightly soluble in cold water, but dissolves in its own

weight of boiling water, recrystallising on cooling in fine white needles. By prolonged contact with water, it is decomposed. It is freely soluble in alcohol and in ether in the cold. In acetic acid, benzene, chloroform, carbon disulphide, and carbon tetrachloride, it is only slightly soluble in the cold, soluble in boiling. It dissolves in boiling hydrochloric acid, and recrystallises on cooling in transparent needles. On adding a solution of barium hydrate to its ethereal solution, a deep blue coloration is obtained. With solution of sodium sulphite, it gives a red coloration, which is fugitive. It is decomposed by concentrated nitric acid with evolution of nitrous fumes. It dissolves in cold concentrated sulphuric without evolution of gas; on warming it is decomposed, with blackening and evolution of hydrochloric acid. The conversion of trichloropyrogallol by condensation into leucogallol, was effected by treating the finely powdered substance with chloroform or carbon tetrachloride, which had been previously saturated with chlorine. At first a wine-red coloration was produced, and effervescence then ensued, the colour changing to a clear yellow. The reaction is complete in about 10 minutes. After allowing the solvent to evaporate, a crystalline residue was obtained, which was identified as leucogallol.

If, on the other hand, the original phenol be added to the chloroform saturated with chlorine gas, these changes rapidly succeed one another, the product consisting of leucogallol, together with a small quantity of the trichloro-compound, which was separated by taking advantage of its solubility in a mixture of 3 parts benzene and 1 part ether.

Under the conditions adopted for the preparation of the trichloropyrogallol, above described, it is evident, however, that the formation of this compound constitutes a distinct stage in the progressive action of chlorine upon the phenol; on one occasion only did I obtain, crystallising from the mother-liquors, a small quantity of one of the higher derivatives (mairogallol) obtained by Stenhouse and Groves.

Tribromopyrogallol.—Stenhouse mentions (**28**, 7) that on heating tannin with commercial bromine (containing water) at 100°, tribromopyrogallol is formed. I find that on allowing bromine to act upon tannin in presence of glacial acetic acid, a very large yield of this compound is obtained. Sufficient of the acid is added to form with the tannin a thick cream; bromine is then added, so long as it continues to be taken up; and, lastly, the mixture is heated on the water-bath for an hour, care being taken to keep the bromine in excess. On setting the liquid aside to cool, the whole solidifies to a mass of needles of the tribromo-compound. A portion was analysed after recrystallisation from benzene:—

0·3620 gave 0·5544 AgBr and 0·0023 Ag.

University of Illinois

	Calc. $C_6Br_3(OH)_3$.
65·6 per cent. Br.	66·1

The mother-liquor was found to contain a certain proportion of brominated products of condensation. On distilling at 100° the tubulus of the retort became filled with a substance crystallising in large oblique rhombohedrons, and having the properties of bromyl hydrate.

This method of preparing tribromopyrogallol would seem to be more economical than the ordinary one of treating pyrogallol itself with bromine.

In the course of my investigation I also had occasion to repeat the observations of Stenhouse and Groves (*loc. cit.*) on the formation of the more complicated derivatives resulting from the action of the halogens upon pyrogallol. It may be of interest to record certain of the results.

Mairogallol.—By the method described by the above chemists (**28**, 706), the yield of crude substance is stated to be 25—30 per cent. "in a properly conducted operation." By the following method I have obtained a yield of mairogallol exceeding 50 per cent. of the pyrogallol employed. 15 grams of the dry pyrogallol are treated with 45 grams of strong acetic acid (60 per cent.) in a tube; and a rapid current of chlorine is passed through the mixture, kept cool by cold water. After about 20 minutes, during which the mixture has passed through various changes of colour, effervescence occurs, the colour of the solution changes from purple to yellowish-brown, and the reaction is soon completed. The solution is set aside for 24 hours, some quantity of the mairogallol crystallising out; a small quantity of strong hydrochloric acid is then added, and the solution again set aside, when the remainder of the mairogallol crystallises out. From 15·55 grams of pyrogallol I obtained in this way 7·85 grams of mairogallol.

It is evident therefore that the application of heat, recommended by Stenhouse and Groves, is to be avoided.

Leucogallol.—In preparing this compound according to their method, I have always obtained, in addition to mairogallol, some quantity of the trichloropyrogallol described above.

Xanthogallol, $C_{18}H_4Br_{14}O_6$.—I have prepared this compound from tribromopyrogallol according to the method of Stenhouse and Groves, also the derivative $C_{18}H_7Br_{11}O_9$, formed by the action of alkalis upon the above compound, and can confirm the statements of these chemists in every particular.

In conclusion, I may mention that I am continuing these investigations, together with Messrs. Cross and Bevan, in the direction already indicated. We are also studying the action of the halogens upon phloroglucol.

ANNIVERSARY MEETING,

March 31st, 1884.

Dr. W. H. Perkin, F.R.S., in the Chair.

The following Report was read by the President:—

In accordance with our bye-laws, I have the pleasure of submitting to you the following Report on the present condition of our Society.

In numbers, I am glad to say that the Society continues to increase. At the last Annual General Meeting we had 1247 Fellows. Since then 119 have been elected and have paid their admission fees; but the Society has lost by death, resignation, and removals, 40 Fellows; therefore, our present number of Fellows is 1326, being an increase of 79, while that of the previous year was 72.

The present state of the Society is set forth in the following tabular form:—

Number of Fellows (Annual General Meeting), March 30th, 1883	1247
Since elected	119
	1366
Losses by death, resignation, and removals	40
Present Number of Fellows, Mareh 31st, 1884	1326
Increase = 79.	
Number of Foreign Members at last Anniversary	36
The present number is the same.	

I regret to have to announce that the losses sustained by the Society by death have been exceptionally great: they number 19, and include some of our oldest and some of our most illustrious Fellows. Their names are:—R. R. F. Davey; William Grant; William Griffin; James Hogarth; G. M. Hopwood; Edward Hurst; C. H. Hutchinson; W. A. Peake; Thomas Pearsall; William Plunkett; G. B. Robertson; General H. Y. D. Scott; Peter Spence; Sir C. W. Siemens; Francis Slinger; J. Hill Smith; William Spottiswoode; J. T. Way; and James Young.

During the past year it became necessary, as well as our duty, to clean and redecorate the Society's rooms. The matter was entrusted to a Committee, and the work was carried out during the summer recess.

Our Library has been, as usual, constantly receiving fresh additions of books, and the Library Committee have also been using their best efforts to complete any imperfect sets. The Editor and the Committee have been engaged for some time with the laborious work of preparing a new Library Catalogue. On account of this, and also of the derangement of the premises by the decorators, it was found necessary to close the Library for a few weeks, and to stop the issue of books for a still longer period. It is feared that this must have caused inconvenience to many of our Fellows; it was however unavoidable. It is hoped that the new Catalogue will be completed by about the end of the present session.

The Collection of the Autotype Portraits of your past Presidents is now nearly completed, through the energy of your Treasurer, who, in his thoughtfulness for the interests of the Society, first proposed that this collection should be made. They are hung in the Council Room, where they can be seen by the Fellows.

It will be remembered that when Dr. Longstaff so liberally gave the Society £1000 for the purpose of starting the Research Fund, he made a special condition, viz., that a medal should be awarded at least every three years to the Fellow of the Society who, in the opinion of the Council, had done most to promote Chemical Science by research since the period of the last award. The first award was made to Professor Thorpe in 1881. Another three years have therefore passed, and it has become the duty of your Council to consider this matter again; and in doing so they have agreed that Mr. O'Sullivan be the recipient of the medal this year.

Mr. O'Sullivan—It gives me great pleasure to present to you the Longstaff Medal awarded to you for your important and laborious researches on the carbohydrates. The methods you have used for the purpose of getting an insight into the complicated structure of many of these compounds by gradually breaking down the molecule and examining the resulting products, has thrown much light upon their constitution. The methods of determining starch and the investigation of the α- and β-amylan, the constituents of some cereals, are also subjects of considerable interest and utility. It is hoped that this recognition of your labours may encourage you in your work, and that ere long we may receive fresh communications from you.

I feel there is a special interest connected with the award of this medal to-night, as this is the eighty-fifth birthday of our esteemed and highly valued friend, Dr. Longstaff. He is now one of the few remaining original Members of the Society. We trust, however, that he may still be spared to see this medal awarded many times more, and also his desire realised both in connection with this and in connection with the Research Fund, which he also founded: namely,

that they may help to stimulate the love of research amongst our Fellows, and that important work may be done to promote the advancement of our science.

The following is a list of the Papers read before the Society between March 30th, 1883, and March 31st, 1884. About half of these refer to so-called Organic Chemistry; the other half to Inorganic Chemistry and general subjects:—

I. "On the Estimation of Hydrogen Sulphide and Carbonic Anhydride in Coal-gas:" by L. T. Wright.

II. "Contributions to the Chemistry of the Cerite Metals:" by B. Brauner.

III. "Some Compounds of Antimony and Bismuth containing Two Halogens:" by R. W. Atkinson.

IV. "On the Gases evolved during the Conversion of Grass into Hay:" by P. F. Frankland and F. Jordan.

V. "Note on an Apparatus for Fractional Distillation under Reduced Pressure:" by L. T. Thorne.

VI. "On the Condition in which Carbon exists in Steel:" by Sir F. A. Abel and W. H. Deering.

VII. "On the Spectrum of Beryllium, with Observations relative to the Position of that Metal among the Elements:" by W. N. Hartley.

VIII. "On a New Oxide of Tellurium: On Tellurium Sulphoxide, and on a New Reaction of Tellurium:" by E. Divers and M. Shimosé.

IX. "A Simple Modification of the Ordinary Methods for effecting the Combustion of Volatile Liquids in Glaser's Furnace with the Open Tube:" by Watson Smith.

X. "On the Production of Ammonia from the Nitrogen of Minerals:" by G. Beilby.

XI. "On the Specific Gravity of Paraffin Wax, Solid, Liquid, and in Solution:" by G. Beilby.

XII. "Laboratory Notes. (1.) On the Action of Light and Heat on Cane and Invert Sugars. (2.) On Hydroxylamine. (3.) On the Recovery of Iodine from Organic Iodine Residues. (4.) A Residual Phenomenon of the Electrolysis of Oil of Vitriol:" by J. H. Gladstone and Alfred Tribe.

XIII. "On an Alleged Test for Alcohol. On the Reaction of the Copper-zinc Couple on Nitric Oxide. On the Reducing Action of Spongy Lead:" by J. H. Gladstone and A. Tribe.

XIV. "Note on a Basic Ammonia-copper Sulphate:" by S. U. Pickering.

XV. "Notes on Loew and Bokorny's Researches on the probable Aldehydic Nature of Albumin:" by A. B. Griffiths.

XVI. "Note on the Action of Sulphuric Acid (sp. gr. 1·84) upon Potassium Iodide:" by H. Jackson.

XVII. "Action of Nitrous Anhydride on Glycerol:" by O. Masson.

XVIII. "On Evaporation in Vacuo:" by H. McLeod.

XIX. "On the Preparation of the Pentathionates:" by S. Shaw.

XX. "Note on Pentathionic Acid:" by Watson Smith.

XXI. "Note on Hydrocarbons from Camphor:" by H. E. Armstrong.

XXII. "On the Rate of Decomposition of Ammonium Nitrate:" by V. H. Veley.

XXIII. "On a New Gas-burner for Heating Gas-tubes:" by W. Ramsay.

XXIV. "Note on the Action of Allylic Iodide upon Phenol in the Presence of Zinc or Aluminium:" by P. F. Frankland and T. Turner.

XXV. "On a Bye-product of the Manufacture of Aurin:" by A. Claparède and Watson Smith.

XXVI. "On Samarium and its Compounds:" by P. T. Clève.

XXVII. "On Homologous Spectra:" by W. N. Hartley.

XXVIII. "On Thioxalic Ether:" by H. F. Morley and W. Johnston Saint.

XXIX. "On the Condensation-products formed by Benzoic Aldehyde with Malonic and Isosuccinic Acids:" by C. M. Stuart.

XXX. "A Contribution to the History of the Constitution of Bleaching Powder:" by L. T. O'Shea.

XXXI. "Researches on Secondary and Tertiary Azo-compounds. No. 1:" by R. Meldola.

XXXII. "Chemistry of Lacquer (Urushi). Part I:" by Hikorokuro Yoshida.

XXXIII. "On the Formation of Hydroxylamine from Nitric Acid:" by Dr. E. Divers.

XXXIV. "On Some Compounds of Phenols with Amido-bases:" by G. Dyson.

XXXV. "On the Alleged Decomposition of Phosphorous Anhydride by Sunlight:" by R. Cowper and V. B. Lewis.

XXXVI. "On the Estimation of Starch:" by C. O'Sullivan.

XXXVII. "On the Illuminating Power of Ethylene when burned with Non-luminous Combustible Gases:" by P. Frankland.

XXXVIII. "On the Products of Decomposition of Aqueous Solutions of Ammonium Nitrate:" by G. S. Johnson.

XXXIX. "On the Estimation of Iron by Potassium Bichromate:" by E. B. Schmidt.

XL. "On the Constitution of Fulminates:" by E. Divers and M. Kawakita.

XLI. "Theory of the Constitution of the Fulminates:" by E. Divers.

XLII. "On Liebig's Production of Fulminating Silver without the use of Nitric Acid:" by E. Divers and M. Kawakita.

XLIII. "Note on the Constitution of the Fulminates:" by H. E. Armstrong.

XLIV. "Experimental Investigations on the Value of Iron Sulphate as a Manure for Certain Crops:" by A. B. Griffiths.

XLV. "Researches on the Gums of the Arabin Group. Part I. Arabic Acid, its Composition and the Products of its Decomposition:" by C. O'Sullivan.

XLVI. "On the Decomposition of Ammonia by Heat:" by W. Ramsay and S. Young.

XLVII. "On the Halogen Compounds of Selenium:" by J. P. Evans and W. Ramsay.

XLVIII. "On the Preparation of Pure Chlorophyll Pigments:" by C. Tschirch.

XLIX. "On Camphoric Peroxide and Camphorate of Barium:" by C. T. Kingzett.

L. "Supplementary Note on Liebig's Production of Fulminating Silver without the use of Nitric Acid:" by E. Divers and M. Kawakita.

LI. "On the Decomposition of Silver Fulminate:" by E. Divers and M. Kawakita.

LII. "On Hyponitrites:" by E. Divers and Tamemasa Haga.

LIII. "On the Expansion of Liquids:" by D. Mendelejeff: translated from the Russian by B. Brauner.

LIV. "Researches on Secondary and Tertiary Azo-compounds. No. II:" by R. Meldola.

LV. "On the Nitrogenous Matters in Grass and Ensilage from Grass:" by E. Kinch.

LVI. "On the Influence of the Temperature of Distillation on the Composition of Coal-gas:" by L. T. Wright.

LVII. "On the Composition of the Ash of Wheat Grain and Straw Grown at Rothamsted in Different Seasons, and with Different Manures:" by Sir J. B. Lawes and J. H. Gilbert.

LVIII. "On the Analysis of Shotley Bridge Spa Water:" by H. Peile.

LIX. "Studies on Sulphonic Acids. No. 1. On the Hydrolysis of Sulphonic Acid, and on the Recovery of Benzenes from their Sulphonic Acids:" by H. E. Armstrong and A. K. Miller.

LX. "On a Relation between the Critical Temperature of Bodies and their Thermal Expansions as Liquids:" by T. E. Thorpe and A. W. Rücker.

LXI. "Remarks on the Densities of Members of Homologous Series:" by W. H. Perkin.

LXII. "Note of some Experiments made at the Munster Agricultural School, to determine the Value of Ensilage as a Milk and Butter-producing Food:" by T. Farrington.

LXIII. "Note on the Behaviour (1) of the Nitrogen of Coal-distillation, and (2) a Comparison of the Amounts of Nitrogen left in Cokes of various Origins:" by Watson Smith.

LXIV. "On a hitherto Unnoticed Constituent of Tobacco:" by T. J. Sorery.

LXV. "Note on the Preparation of Marsh-gas:" by J. H. Gladstone and Alfred Tribe.

LXVI. "On the Action of Dibrom-α-naphthol upon Amines:" by R. Meldola.

LXVII. "Note on the Existence of Salicylic Acid in the Cultivated Varieties of Pansy and the Violaceæ generally:" by A. B. Griffith and E. C. Conrad.

A Lecture was delivered by Captain Abney, F.R.S., "On Photographic Action Studied Spectroscopically."

It would be out of place here to attempt to give anything like a complete account of the work which has been done in chemistry during the past year. I will, however, venture to make a few remarks on the subject. The development of chemical science has not slackened, especially on the Continent, as is seen from the *Berichte* of the Berlin Chemical Society, which forms a more and more formidable publication every year. On looking over the researches which have been made, it is interesting to notice that workers have been engaged in apparently all parts of the field of Chemistry, and a good deal on that border-land where Chemistry and Physics merge into each other.

The important subject of "atomic weight" determinations has deservedly received great attention within recent years. Following upon G. F. Becker's "Digest of atomic weight determinations, published since 1814," and Professor Frank Wigglesworth Clarke's "Recalculation of the atomic weights," for the publication of both of which we are indebted to the Smithsonian Institute, Lothar Meyer and Jeubert's independent revision of the original data will be of great value to chemists.

Of new determinations, that of tellurium, by one of our Fellows, Dr. B. Brauner, now in Prague, is of great interest in connection with

the so-called Periodic Law. It is well known that tellurium was placed by Mendelejeff before iodine, although the then accepted weight was higher than that of iodine. Mr. W. L. Wills, in a paper published in our Journal (Trans., 1879, 704), expresses an opinion adverse to this arrangement, but it is noted that his values do not exhibit a satisfactory degree of accordance. Dr. Brauner has devoted special attention to the preparation of pure tellurium, and the discovery of errors latent in the methods employed. The values he has obtained by three independent methods lie between the limits 124·94 and 125·4, so that 125 may be accepted as the probable value, thus giving to tellurium the position which Mendelejeff had assigned to it. Newlands also classified it in his table as below iodine (*Chem. News*, 1864, 459 and 94).

Another illustration of the consistency of the Periodic Law is afforded by titanium. Rose, in 1829, obtained for this element the values 48·13—49·48, and Pierre, in 1847, the value 50·25. Mendelejeff preferred 48, but Pierre's number was more commonly accepted. Professor Thorpe, as the result of three series of determinations, arrives at the conclusion that 48 is the true value.

Professor Dewar and Dr. Scott's experiments have led to the value 55·038 for manganese (*Proc. Roy. Soc.*, 1883, **35**, 44), and it must be with great satisfaction that these chemists have found that the veteran Marignac has obtained substantially the same number (55·07).

Marignac has also redetermined several other atomic weights. According to his experiments, that of magnesium is 24·38; that of zinc is 65·33, if oxygen be taken as 16; that of bismuth 208·16 (S = 32·06) (*Arch. d. Sciences Phys. et Nat.* [3], **10**, 5 and 193). It is interesting to note that F. W. Clarke, by combining all the values which have been obtained for magnesium, arrives at the number 24·014, and that Meyer and Jeubert give 23·94 (H = 1).

Baubigny has arrived at the same value for zinc as Marignac. This chemist has also determined the atomic weights of copper and nickel, finding for the former the value Cu = 63·468, and for the latter Ni = 58·748. His experiments also furnish valuable information on the stability of various sulphates.

Brauner has published in our Journal additional evidence in support of the number 145 (about) for didymium (Trans., 1883, 278). Our foreign Fellow, Professor Cleve, in a paper which greatly adds to our knowledge of samarium, gives data which lead to the value 150 as the atomic weight of this element. He has also redetermined that of lanthanum, La = 138·019, O = 15·963, his results confirming those of Brauner. He has also determined that of yttrium, which he makes 88·9.

From the experiments of Jörgensen the atomic weight of rhodium

is a little lower than that usually accepted, Rh = 103·4 (*Ber.*, **16**, 1058).

Bougartz has also made fresh observations on the atomic weight of antimony; his results closely agree with those obtained by Cooke in 1873. The fresh determination of the atomic weight of thorium by Nilson, gives Th = 116·2 (O = 16, S = 32, *Compt. rend.*, **95**, 729—730), this number being a little higher than that obtained by Delafontaine in 1863, viz., 115·72.

The question whether Prout's hypothesis respecting atomic weights or some modification of it, is applicable, has frequently been under discussion of late years. Professor Dewar and Dr. Scott have lately pointed out a method of experimentally dealing with this question, which promises to furnish valuable information; it consists in accurately determining the molecular weight of a compound, the body chosen by them being triethylamine (*Proc. Roy. Soc.*, **35**, 347).

It is not long since we heard with astonishment of the achievements of Cailletet and Pictet in reducing oxygen and hydrogen to the liquid state, thus depriving these gases for ever of the title of "permanent." That we may expect further advances in this direction is evident from a recent communication to the Vienna Academy, which bears the title, "On the use of boiling oxygen as a refrigerating medium, on the temperature produced thereby, and on the solidification of nitrogen." The boiling point of oxygen is approximately estimated at — 186°. When nitrogen compressed in a tube surrounded with liquid oxygen which has been cooled by boiling off, is allowed to expand, it solidifies in snow-like flocculi, consisting of crystals of remarkable size. Wroblewski liquefies oxygen under pressure at the temperature produced by the evaporation of liquid ethylene, *in vacuo*, and estimated at about — 136°. Liquid oxygen is a colourless and transparent liquid, like carbon disulphide, and forms a beautiful meniscus. Another long-cherished idea must also now be abandoned, it seems, for both alcohol and carbon disulphide, when cooled with boiling ethylene, become solid, the former at about —130°, the latter at about — 116° (*Monatsh.*, 1883, 336).

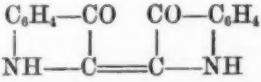
Hydroxylamine, which even now is barely mentioned in our text-books, is rapidly becoming an important analytical reagent, owing to the recent interesting discoveries of Victor Meyer and his pupils. It would seem that in all compounds in which carbonyl is associated with hydrogen or hydrocarbon radicals (as in the aldehydes, ketones, and quinones, &c.) the oxygen-atom is exchanged for the radical N.OH under the influence of hydroxylamine. Moreover, the compounds which have hitherto been regarded as nitroso-derivatives, appear to be compounds containing the radical N.OH, it being probable that even nitroso-phenol is a derivative of ordinary quinone of

the formula $C_6H_4O(NOH)$, since it can be formed by acting on quinone with hydroxylamine (Goldschmidt, *Ber.*, **17**, 213). Should this prove true, the question of the constitution of the quinones, which has so long been a disputed point amongst chemists, will probably receive a definite answer.

The use of hydroxylamine has caused fresh work to be undertaken in reference to its preparation. Carstanjen and Ehrenberg discovered its production from mercury fulminate by hydrochloric acid; this was followed by Steiner; and more recently by one of our Fellows, Dr. Divers, and M. Kawakita, at Tokio, in Japan, who have carefully studied the reaction, and showed how the substance can be made to give good yields of hydroxylamine.

Another analytical reagent of equal importance with hydroxylamine, and which, on account of the readiness with which it can be prepared, will probably often be preferred, is the phenylhydrazine of Emil Fischer. This chemist has pointed out that phenylhydrazine reacts with a large number of ketonic compounds, in many cases forming highly characteristic derivatives; he has very recently described a series of bodies formed by its action on dextrose and other carbohydrates, which promise to be of great interest.

Professor Baeyer has been continuing his important researches on the constitution of indigo, which have led to the discovery of such a number of remarkable and important new products. He has now come to the conclusion that the constitution of this colouring-matter may be represented thus:—



Although there are now several processes by which this important colouring-matter can be manufactured, up to the present time but little has been done in that direction, as it cannot as yet be produced at a sufficiently low price to compete with the natural product. It is, however, used to a small extent by calico-printers on the Continent.

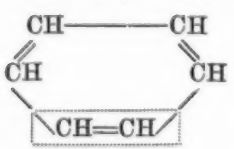
Some very interesting work was done in 1882 by Leukowitsch on mandelic acid. By sowing a solution of the ammonium salt of the inactive acid with various microzoa, he found that it gradually developed dextro-optical activity (*Ber.*, **15**, 1505). Since then he has shown that, by combining the inactive acid with cinchona, and crystallising the product, two salts are obtained, the one containing a lævo- and the other a dextro-mandelic acid, and that these acids, like the corresponding tartaric acids, when mixed, reproduce the inactive acid. The lævo- acid also, when heated to 160° for 30 hours, is converted into benzaldehyde and the inactive acid, which can in its turn be split up into the lævo- and dextro-bodies (*Ber.*, **16**, 1568—1577).

Solutions of ammonium glycerate and ammonium lactate, when subjected to the influence of *penicillium glaucum* for several weeks, became optically active, the glycerate solution becoming lævo- and the lactate dextro-gyrate.

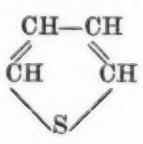
A remarkable feature in the history of chemistry is the great increase of our knowledge of quinoline-derivatives, and of allied nitrogenous compounds, during the very few years which have elapsed since Skraup's important discovery of the synthetical method of preparing quinoline. On all sides we hear of condensations being effected which lead to the production of pyridine or quinoline-derivatives, and the additions to the list of indol-derivatives are also very numerous.

Dr. Hofmann, by persevering with his process of intramolecular change which takes place on heating the methylated monamines, the methyl changing place with an atom of hydrogen of the radical (a process which has received practical application), has succeeded in replacing all the hydrogen-atoms of the phenyl in aniline, and has thus obtained a pentamethylaniline, $C_6(CH_3)_5.H_2N$.

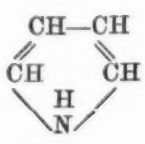
The discovery of Victor Meyer that the colouring-matter which is produced on treating isatin with coal-tar benzene and sulphuric acid is due to the existence in the benzene of the remarkable compound thiophene, is of considerable interest. This substance, in many particulars, resembles benzene. It is a colourless oil boiling at 84° C., yielding bromo-derivatives very similar to bromo-benzenes; it also yields a sulpho-acid and a cyanide, similar to benzonitrile, and this again yields an acid very like benzoic acid. Thiophene is an interesting compound also on account of its power of forming colouring-matters with a variety of substances, such as isatin, already mentioned, phenylglyoxylic acid, phenanthraquinone, benzyl, and alloxan; and from the experiments which have been made it appears likely that this substance will serve as a valuable agent in differentiating double ketones of the benzyl and phenanthraquinone type, in which the two carbonyls are in direct association, from those in which the carbonyls are but indirectly associated, as in anthraquinone. Victor Meyer has also made the interesting observation that pyrrol acts like thiophene in this particular, and from his observations it appears that these bodies may, in all probability, be represented as benzene, in which one of the three acetylene-groups is replaced by S or NH, thus:—



Benzene.



Thiophene.



Pyrrol.

There appears also to be a whole series of thiophenes in coal-tar, corresponding to the homologues of benzene. The existence of methyl-thiophene, the toluene of the series, has already been established by the preparation and analysis of its bromine-derivative.

Krafft's recent discoveries of the higher olefines, $C_{12}H_{14}$, $C_{14}H_{28}$, $C_{16}H_{32}$, and $C_{18}H_{36}$, are a welcome addition to his previous important contributions to our knowledge of the higher normal paraffins.

I feel I must not pursue my remarks on these matters further, although there are such a number of important subjects which deserve to be considered, that it makes it difficult to conclude this short review; but doubtless the subjects I have referred to will call many others to your mind, and thus will serve the purpose intended, viz., that we may realise to some extent the very large amount of important work which is being carried on in connection with our Science.

Last year my predecessor, in his address, referred to the increasing number of chemical laboratories in the United Kingdom, and the greater facilities which are now afforded for the prosecution of research. After considering the number of papers which have been read before this Society during the past few years, it appeared to me that it might be useful to make some remarks as to the influence these greater facilities have had on the development of Chemical Science.

The first thing that attracts attention is the startling and anomalous fact, that the number of papers read before the Society (and I think this may be taken as a good criterion, especially as but few have been brought before the Royal Society) is declining year by year. The largest number we ever had was in the session 1880—81, when there were 113 communications brought before us; but in 1881—82 they declined to 87, in 1882—83 to 70, and this last session to the lamentably low number of 67, or about the number we had nine years ago. And this, not only with increased laboratory accommodation, but also with the assistance offered to investigators by our Research Fund and the Government Grant. This state of things causes us to look around and see where research *is* and where it *is not* being carried on in the United Kingdom.

If we look to the laboratories of our Universities, from many of these we never hear of a research emanating, and from the rest, taken as a whole, we get but driblets at intervals. How different to the German Universities, from which there is such an incessant flow of work!

If we turn to the other laboratories connected with our Colleges, Hospitals, &c., with how few exceptions do we find any appreciable amount of work being carried on for the extension of the boundaries of our Science; in fact, speaking in a general way, the work of our

laboratories consists mainly in the students carrying out the ordinary course of qualitative and quantitative analysis, and attending one or two courses of lectures.

It is scarcely necessary to say that this is not sufficient, however well taught, to make a student a chemist; it is but a preliminary part of the training, which, being carried on as it usually is, by tables, and carefully laid down directions, gives but little scope for independent thought and action. The subsequent prosecution of scientific research, under proper supervision, however, is quite another thing, and calls out all the faculties of the student, requiring, as it does, independent thought and independent methods of working, and, moreover, gives him an insight and vivid interest in his science that nothing else will do. The preparation of chemical products, before the commencement of research, is no doubt also a very useful training if sufficiently diversified; but research is the most important of all.

The degree of Doctor of Philosophy has undoubtedly done a good deal to further Chemistry in Germany, necessitating, as it does, the prosecution of original work, and now that degrees are so much thought of in this country (though why a chemist with one of our ordinary University degrees should be preferred to one who has fully given his mind to his Science, and therefore has not got such a degree, it is difficult to understand), it is believed that if something analogous to the Ph.D. could be inaugurated in this country, it would help to further Chemical Science here also. A step in this direction has been taken at the Owens College, Manchester, but hitherto the degree has not found favour with students. It is not surprising, however, while there are so many different degrees not requiring original work as a *sine quâ non*, that such a degree should not be sought after. This difficulty, however, might be overcome by modifying the requirements for the present degrees, and requiring that original research should be substituted for book knowledge. At the London University original work is recognised, but not required.

The past neglect of research will, it is to be feared, have a more lasting influence on the progress of chemistry in this country than may appear at first sight, and in this way. Those who have been students in laboratories where the importance of this kind of work is not recognised, advance in their positions, becoming Assistant Demonstrators, &c., and eventually Professors, and as they have not learnt to practically realise the value of research by being in the habit of conducting it themselves, or of seeing others do so, when they become Professors they will naturally not encourage students to undertake it in their laboratories, and it is to be feared that we are already suffering in this way, and that this is one of the causes why the new labora-

tories which have been opened are doing so little to add to our store of fresh knowledge.

It is said that students cannot be induced to stay longer than is necessary to go through the ordinary course of qualitative and quantitative analysis, and can this be wondered at when they do not see anything else going on of sufficient interest to make them feel it would be a great advantage for them to do so? Would it be the case if higher work were being enthusiastically carried on? The fact that many of our students are found to leave this country and go to Germany, where research is carried on with so much zeal, I think gives an answer to this question.

In all chemical laboratories there are, without doubt, different classes of students, some who have no right to be there, having no care for science; those who have not sufficient capacity to proceed with its study beyond an elementary stage; and those who are capable of becoming efficient chemists. Of course it would be but waste of time to attempt to make the first two classes remain and engage in research. It is to be feared, however, that some are not unfrequently thought to belong to the second class who really, if sufficiently interested in their science by the example of others, would be found to be possessed of no mean ability. When a young man is made to realise that he may be the discoverer of new facts, or does discover new facts, he gets a new impulse, which alters the whole current of his thoughts and actions.

There can be no doubt that when a Professor, his assistants, and advanced pupils are enthusiastically engaged with research, their influence is found to act even on beginners, who, if they possess any scientific spirit at all, will realise that the ordinary course of analysis is but a preliminary thing, and will thus be induced to use their best energies to master it that they also may try their hand at original work.

That this condition of things is calculated to fill laboratories with students is seen from the fact that on the Continent, where the greatest scientific activity prevails, the laboratories are the most crowded, and this is the kind of activity we want in this country, where our students pre-eminently possess all the faculties for original work, but as they are not cultivated these are not developed.

There is also another class of students who study chemistry, but the fruit of their study is so extremely small, that it is difficult to realise that it possesses any practical value. I refer to medical students; yet there are good teachers and good laboratories employed in the work, in fact a very large amount of valuable power is used for it; but it seems almost like the employment of a large amount of power to raise a weight to a certain distance and then let it fall again,

and year after year to continue the same thing, never raising it sufficiently high that it may be placed in a useful position. The present condition of things cannot but be disheartening both to students and to teachers. Medical students have so much to learn that it is sad they should have to waste their time in studying chemistry in the way they do. If there is any value in chemical products as curative agents, if there is any value in physiological chemistry, or any importance in toxicology, surely medical students should have a sound knowledge of chemical science, and not simply learn to detect an acid and a base in a mixture, an operation which is of no value except as an intermediate exercise, to be followed by more advanced work.

The only cure for the evil appears to be either that their term of study should be lengthened, or that other subjects which are of less importance should be withdrawn from the curriculum, so as to enable them to work at this science sufficiently. Unfortunately medical men have as a rule acquired so imperfect a knowledge of chemistry themselves, that they have found it to be of little value, and therefore do not sufficiently see how important its proper study would be to students. It is evidently high time that some steps were taken to economise the present waste of time and power, and that we should hear of some good work proceeding from the numerous, and in many cases well appointed chemical laboratories connected with our hospitals.

Of late years much attention has been given to the subject of technical or applied chemistry, and it is to be hoped that this movement will be so judiciously carried on that much will be done for perfecting and developing the chemical manufactures in this country; but it appears that there is an idea in the public mind that there are two kinds of chemistry in existence, one suitable for the manufacturer, and the other suitable for the scientific man; and unless this idea can be successfully eradicated, it is to be feared that much of the value of this movement will be lost, and we shall be left in the position of followers instead of leaders; copyists of what others are doing, instead of being originators of new processes and industries.

In the present state of things students who are to be manufacturers are supposed to know enough chemistry when they have acquired a knowledge of ordinary analytical methods, and the result is that we have but very few efficient chemists in our works. On the Continent, however, we find a very different state of things: first of all in their chemical works they usually have a much larger staff of chemists than we do, and secondly, their chemists are efficient men.

The chemists preferred in Germany are those who have had a thorough training, and taken their degree of Doctor of Philosophy, and shown their power as chemists by conducting original research,

and in many cases have been for some time assistants to the Professors in their research laboratories. Those from the Polytechnics are not so much valued, except in relation to their knowledge of engineering, mechanics, &c.

What do we see as the result of the employment of high class chemists in Germany? First, we notice that chemical industries are developing and increasing there more than in any other country; and secondly, that the manufacturers are able to make their products in a very economical manner, and as a consequence supply them at a low price. Men who have studied chemistry sufficiently to do analysis and look after existing processes which are well known, are certainly useful in their way; but we want more than this; we want men who have had their minds so trained by carrying on research, that they may be imbued with a spirit of investigation, and be able to improve or entirely change processes in use, and to keep up their knowledge of chemical science, so as to be able to grasp the importance of new scientific facts, and make them subservient to the industries they are engaged in.

The chemists from the German Universities, when entering chemical works, naturally have but little knowledge of technical processes. This they have to acquire, but unfortunately they then only are likely to see those operations which are carried on in the particular industry to which they become connected. Those who study in the Polytechnics have a certain advantage in this particular, inasmuch as they can become acquainted with processes carried on in a variety of manufactures; and what is wanted now-a-days is something like what would result from a fusion of the work of the Universities and the Polytechnics, *i.e.*, scientific training similar to that in the former, with a general knowledge of engineering, mechanics, &c., and the methods adopted in carrying on processes on the large scale, this latter not being confined to one industry only, but also to industries in general, so that great breadth of knowledge may be acquired. With men so trained we might expect to see our chemical industries flourish, and keep at least abreast of those on the Continent.

It is to be hoped that some such standard of training will be undertaken at the Central Institute of the City and Guilds of London. It would be a sad thing to find the munificence of the City Companies resulting only in perpetuating the present kind of imperfectly trained chemists, who are incapable of advancing the chemical industries of this country, so that our manufacturers not unfrequently find it necessary to send to the Continent for more competent men.

In this retrospect of the work which is being carried on in relation to chemistry, it may be thought by some that an undue weight has been given to that which is going on in Germany, and too little to that

which is being carried on in this country; but I think if any one will impartially compare one with the other, this will not be found to be the case. Science, however, has no nationality, and as chemists we cannot but be thankful that it is being actively studied, whether abroad or in our own country; but we must feel that it is our duty to do our part, especially when we see from the work which has been and is being done in this country, that nationally we have the characteristics which qualify us to take a prominent position in work of this nature.

But from the point of view of our national progress we are bound to be active workers in this field of science. There is no doubt we do not hold the position we did as chemical manufacturers, and unless our chemical industries keep pace with chemical discovery fully as well as they do on the Continent, our position must further decline, and moreover, unless we make chemical discoveries ourselves, we must wait until we hear of the discoveries of others, which will mean, in cases where they are susceptible of practical application, that we are placed at a great disadvantage.

The bearing which the progress of chemistry in this country has upon this the oldest Chemical Society in existence is so obvious, that it is superfluous to make any observation on the subject, except to express the hope that it will continue to be active, and found doing its part for the advancement of our science, and as a consequence be an important factor in the welfare of our country.

The Treasurer stated that the funds of the Society were in a very satisfactory state, the balance in favour of the Society being that year larger than on any previous occasion, and amounting to £830. This large increase over former years is, however, to some extent, merely accidental, as it arises in part from nearly twice as many Fellows having paid the life composition this year as last. Further, the expenses this year are somewhat less than they were last year. The total income of the Society this year was £3,536, and the expenses £2,706.

The amount of grants made from the Research Fund during the year amount to £95, and the income to £264 15*s*.

Dr. THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY FROM MARCH 31, 1899

Dr. The Treasurer in Account with the Chemical Society from March 21, 1883, to March 24, 1884. Cr.

	£	s.	d.	£	s.	d.
Balance at Bank March 21st, 1883	1,194	10	9			
,, in hands of Treasurer	1	11	8			
				1,196	2	5
Receipts by Admission Fees, Subscriptions, and Life Compositions, from March 21st, 1883, to March 24th, 1884.						
23 Life Compositions	460	0	0			
113 Admission Fees	452	0	0			
1 Subscription for 1880	2	0	0			
16 ,, ,, 1881	32	0	0			
63 ,, ,, 1882	123	0	0			
255 ,, ,, 1883	502	0	0			
690 ,, ,, 1884	1,336	0	6			
				2,907	0	6
Sale of Journal and Index				318	4	11
Subscriptions for Proceedings of Royal Society				45	10	0
,, from Institute of Chemistry				7	5	0
Dividend on Consols	117	10	0			
,, Metropolitan Board of Works	110	7	4			
,, London and North Western Railway Debenture Stock	30	16	2			
				258	13	6
				4,732	16	4

Assets.	£	s.	d.
Balance at Bank	1,704	2	11
,, in hands of Treasurer	0	11	8
Three per Cent. Consols	4,000	0	0
London and North Western Railway Debenture Stock	788	0	0
Metropolitan Board of Works 3½ per cent. Stock	3,300	0	0
	9,792	14	7

	£	s.	d.	£	s.	d.
Expenses on Account of Journal.						
Salary of the Editor	250	0	0			
,, Sub-Editor	100	0	0			
Fees to Abstractors	269	19	2			
Periodicals for Abstractors	12	8	9			
Distribution of Journal	123	9	5			
Printing of Journal	835	3	9			
				1,591	1	1
Expenses on Account of Library.						
Salary of Librarian	50	0	0			
,, Library Attendant	62	0	0			
Books and Periodicals	74	12	9			
Binding Books	54	16	3			
				241	9	0
Printing Authors' Copies				25	10	6
Proceedings of Royal Society, and Distributing same				65	1	4
Reports of Meetings				24	0	0
Miscellaneous Printing				47	14	3
Insurance of Furniture and Books				2	0	0
Inhabited House Duty and Income-tax				6	17	6
Stationery, Postage, &c.				34	14	2
Redecorating and Furnishing Society's Rooms				293	18	0
Photographs of Presidents				16	2	4
Collector's Commission on Subscriptions				145	7	0
Treasurer's Stamps and Clerical Aid and Drafts				6	3	0
Amount Paid on Account for new Catalogue				20	0	0
House Expenses.						
Providing Refreshments	21	0	0			
Heating the Building	18	18	0			
Lighting ,,	53	19	10			
Cleaning ,,	20	0	0			
Wages of House Porter	52	0	0			
Petty House Expenses	9	16	9			
Repairs	7	2	6			
Gratuity to Gate Porter	2	2	0			
				184	19	1
Treasurer's Petty Cash Disbursements				1	11	0
Purchase of £300 Metropolitan Board of Works 3½ per cent. Stock				320	13	6
Amount received by Bank in error				1	1	0
Balance at Bank	1,704	2	11			
,, in hands of Treasurer	0	11	8			
				1,704	14	7
				4,732	16	4

Audited and found correct. { W. R. Eaton Hodgkinson, Leonard Temple Thorne, F. Woodland Toms.

March 26th, 1884.

THE TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH THE RESEARCH FUND.
FROM MARCH 21ST, 1883, TO MARCH 24TH, 1884.

DR.

	£	s.	d.
Balance at Bank, March 21st, 1883	166	7	3
Subscriptions and donations	106	1	0
Dividend on North British Railway Stock	38	19	10
„ Metropolitan Board of Works 3½ per cent. Stock	119	15	2
	£431	3	3

CR.

1883.	£	s.	d.
July. Grants made	30	0	0
1884.			
January. Grants made	65	0	0
March 24. Balance	336	3	3
	£431	3	3

Assets.	£	s.	d.
North British Railway 4 per cent. Stock	1,000	0	0
Metropolitan Board of Works Stock	3,500	0	0
Balance at Bank	336	3	3
	£4,836	3	3

Examined and found correct,

March 26th, 1884.

W. R. HODGKINSON,
LEONARD TEMPLE THORNE,
F. WOODLAND TOMS.

XXXV.—*The Influence of Incombustible Diluents on the Illuminating Power of Ethylene.*

By Percy F. Frankland, Ph.D., B.Sc., F.I.C., Associate Royal School of Mines.

The experiments recorded in the present paper form the sequel to a communication which I made some months ago—"On the Illuminating Power of Ethylene when Burnt with Combustible Non-luminous Diluents" (p. 30 of this volume). The ethylene used in these experiments was prepared in the same way, and the photometric method employed was the same as that described in the previous paper.

The diluents experimented with were those which are incidental to the manufacture of coal-gas, viz., carbonic anhydride, nitrogen, oxygen, atmospheric air, and aqueous vapour.

Although it has long been known generally that the presence of carbonic anhydride, nitrogen, or atmospheric air in coal-gas tends to interfere prejudicially with its illuminating power, yet, as far as I am aware, but few accurate and systematic experiments have been carried out or published on this subject.

My experiments have been made with ethylene and not with coal-gas, for several reasons: firstly, in order to render these experiments comparable with my former ones on ethylene; secondly, because ethylene possesses a much higher illuminating power than coal-gas, and therefore renders it possible to trace the influence of the diluents over a wider range; and, thirdly, because ethylene being at all times procurable in a state of almost perfect purity, all the results are comparable *inter se*, which would not be the case with coal-gas, the composition of which is liable to variation, especially after storage in experimental gasholders.

The illuminating power of the gases was in all cases taken when consumed from a "Referee's Burner."

The illuminating power of pure ethylene when burnt from a Referee's burner, I have already shown to be 68·5 candles, calculated for a consumption of 5 cubic feet per hour.

Influence of Carbonic Anhydride as a Diluent.

The carbonic anhydride was prepared by the action of hydrochloric acid on marble, the evolved gas being passed through a wash-bottle containing a strong solution of sodium carbonate to arrest any vapour of hydrochloric acid.

The following photometric observations were recorded for mixtures of ethylene with increasing proportions of carbonic anhydride:—

Percentage.		Candles observed.	Rate.		Candle-power corrected to 5 cubic feet of gas, and 120 grains of spermaceti.
Ethylene.	Carbonic anhydride.		Gas in cubic feet, per hour.	Candles in grains, per hour.	
93·68	6·32	25·96	2·14	110·0	55·52
90·59	9·41	30·10	2·38	98·2	51·81
89·03	10·97	23·05	2·38	124·1	49·98
81·73	18·27	24·00	2·70	115·5	42·81
70·75	29·25	21·82	3·11	113·8	33·23
64·15	35·85	19·08	3·60	120·0	26·52
52·94	47·06	13·14	4·00	107·6	14·74
45·61	54·39	7·48	4·87	117·0	7·49

On reference to the diagram, which is the graphical expression of these observations, it will be seen that the illuminating power of the ethylene undergoes almost uniform diminution as the proportion of carbonic anhydride with which it is mixed is increased. The intrinsic illuminating power of the ethylene, calculated for a uniform consumption of 5 cubic feet of ethylene per hour, irrespectively of the proportion of the diluent, suffers a similar decline, indicated by the dotted curve.

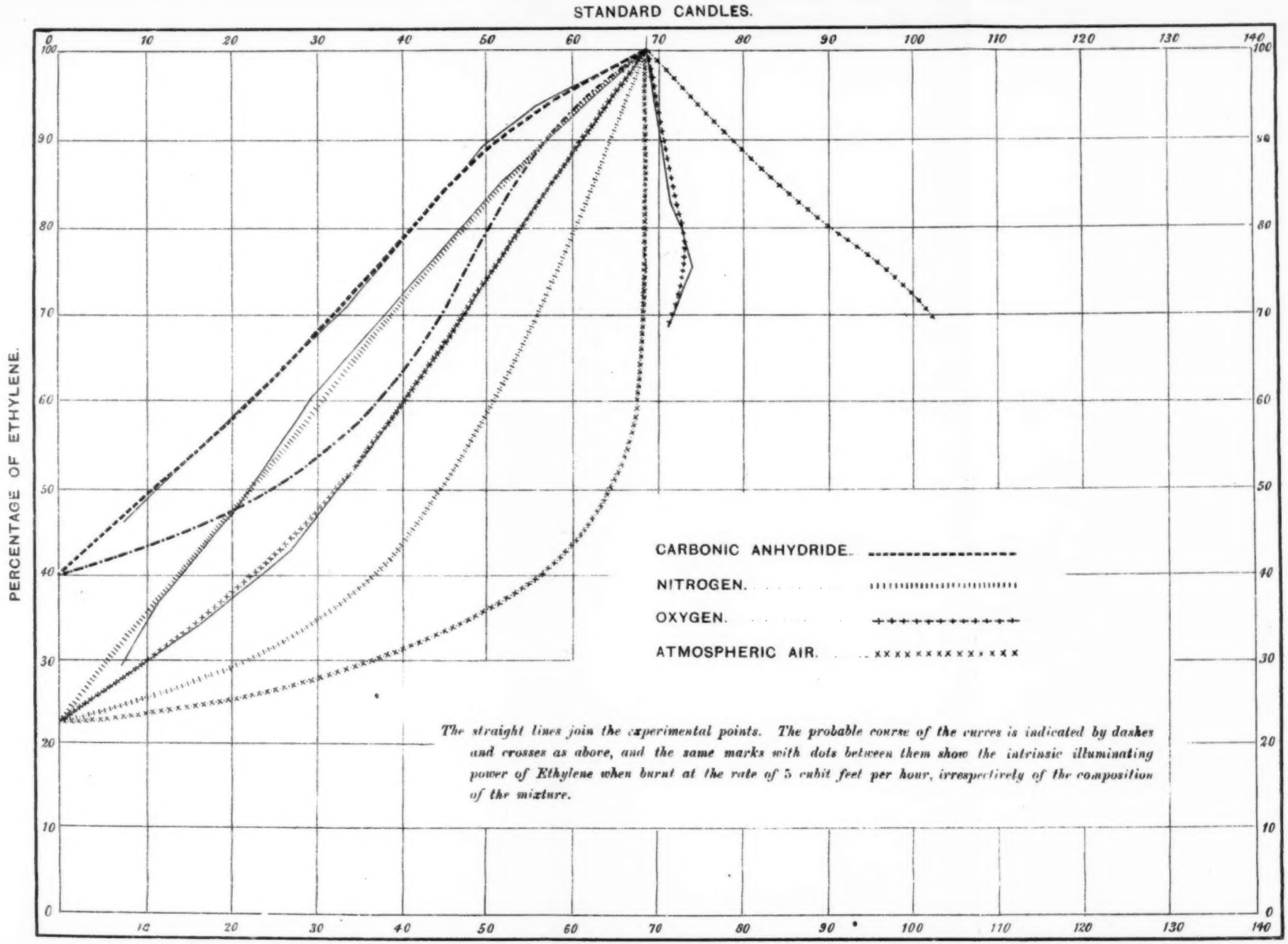
A mixture consisting of about 40 parts ethylene and 60 parts carbonic anhydride burns with a practically non-luminous flame, or in other words the luminosity of ethylene is destroyed on being mixed with $1\frac{1}{2}$ times its volume of carbonic anhydride.

Influence of Nitrogen as a Diluent.

The nitrogen was prepared by heating equal weights of ammonium chloride and sodium nitrate with water in a flask. A little practice is requisite for the successful preparation of nitrogen in this manner; for if the application of heat be not discontinued at the right moment the reaction becomes unmanageable, and the gas is evolved almost with explosive violence. As soon as the evolution of nitrogen is fairly started, the lamp should be removed, and if the reaction becomes somewhat stormy, the flask containing the mixture should be cooled by pouring cold water freely over it; in this manner it is possible to regulate the evolution of gas with great nicety.

The nitrogen, before being collected in a gas-holder, was purified by passage through a saturated solution of ferrous sulphate to remove

ILLUMINATING POWER OF ETHYLENE WHEN BURNT WITH COMBUSTIBLE DILUENTS.


STANDARD CANDLES.
PERCENTAGE OF ETHYLENE.
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140
100 90 80 70 60 50 40 30 20 10 0
CARBONIC ANHYDRIDE.
NITROGEN.
OXYGEN.
ATMOSPHERIC AIR.
The straight lines join the experimental points. The probable course of the curves is indicated by dashes and crosses as above, and the same marks with dots between them show the intrinsic illuminating power of Ethylene when burnt at the rate of 5 cubic feet per hour, irrespectively of the composition of the mixture.

Harrison & Sons, Lith. St. Martins Lane, W.C.

oxides of nitrogen, through strong sulphuric acid to remove ammonia, and through a lime-tower to arrest the carbonic anhydride. The gas yielded on analysis the following results, showing it to be practically pure nitrogen:—

100 *volumes of gas contained*—

Carbonic anhydride	0·05	volumes
Oxygen	0·19	„
Nitrogen	99·76	„
	100·00	„

The following photometric observations were recorded with mixtures of ethylene and nitrogen:—

Percentage.		Candles observed.	Rate.		Candle-power corrected to 5 cubic feet of gas, and 120 grains of spermaceti.
Ethylene.	Nitrogen.		Gas in cubic feet, per hour.	Candles in grains, per hour.	
84·69	15·31	27·74	2·45	110·0	51·96
71·12	28·88	24·06	3·14	124·1	39·58
59·93	40·07	24·36	3·88	113·2	29·64
47·08	52·92	23·18	5·34	115·0	20·81
36·24	63·76	17·22	6·94	114·3	11·82
28·81	71·19	8·82	5·45	107·1	7·20

From these results and the curves in the diagram constructed therefrom, it will be seen that the illuminating power of mixtures of ethylene and nitrogen diminishes almost uniformly as the proportion of nitrogen in the mixture increases. The intrinsic luminosity of the ethylene also suffers a corresponding decline, becoming practically destroyed when the ethylene forms only from 20—30 per cent. of the mixture.

On comparing the results obtained with nitrogen with those for carbonic anhydride, it will be seen that nitrogen exerts a considerably less prejudicial effect than carbonic anhydride upon the illuminating power of the ethylene. The greater disilluminating effect of carbonic anhydride receives its explanation partly in the fact that its specific heat is greater than that of nitrogen, and also to the absorption of heat by its reduction to carbonic oxide in the flame.

Influence of Oxygen as a Diluent.

The oxygen was prepared in the usual manner by heating a mixture of potassic chlorate and manganic peroxide, the evolved gas being

collected in a holder, and then made to pass in a slow stream through a saturated solution of caustic soda to remove any chlorine that might be present.

The combustion of mixtures of ethylene and oxygen is naturally an operation attended with no little danger unless due precautions be taken. Before attempting to consume the mixture from a burner, I collected in each case a test-tube full of the mixed gases, and on applying a light observed whether the gas burnt from the mouth of the tube only or in a body throughout its whole length. As soon as the proportion of oxygen in the mixture was sufficient to cause this latter phenomenon, I deemed it prudent to desist from attempting to make a photometric experiment with the mixture: for although the combination between the ethylene and oxygen in the test-tube was perfectly quiet and noiseless, it is more than doubtful whether this would have been the case if the volume of gas contained in the holder had been operated upon.

In this manner I was able in safety to determine the illuminating power of a mixture containing 31·50 per cent. of oxygen, whilst a mixture with 39·31 per cent. of oxygen was found to be already explosive.

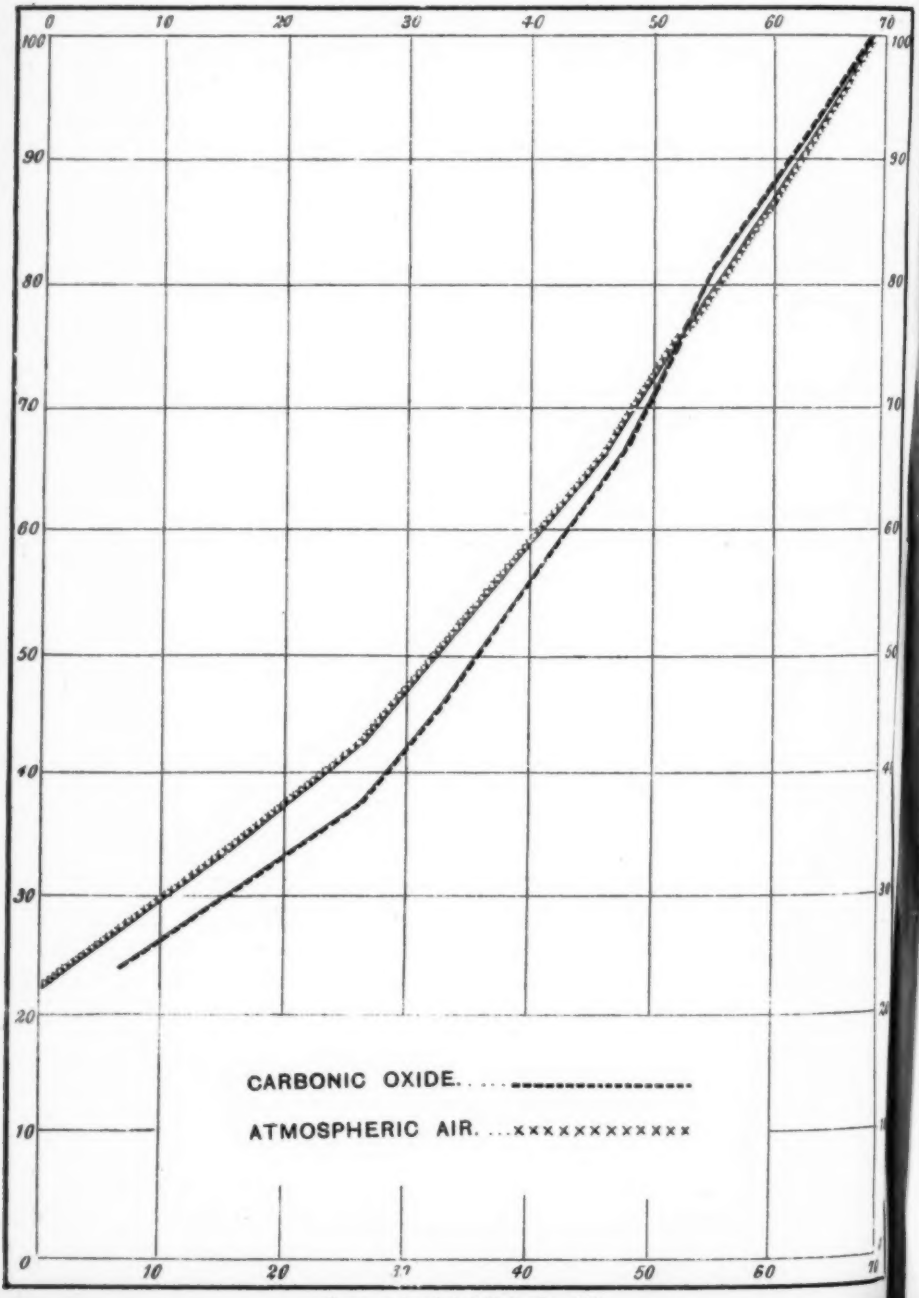
The following photometric obvervations were recorded:—

Percentage.		Candles observed.	Rate.		Candle-power, corrected to 5 cubic feet of gas and 100 grains of spermaceti, per hour.
Ethylene.	Oxygen.		Gas in cubic feet, per hour.	Candles in grains, per hour.	
82·57	17·43	31·70	2·18	117·0	70·93
80·67	19·33	34·52	2·22	111·8	72·52
75·51	24·49	32·98	2·20	118·7	74·19
68·50	31·50	48·26	3·24	114·5	71·17
60·69	39·31	explosive mixture.			

From these results and the curves which are constructed from them, it appears that the addition of oxygen increases the illuminating power of the ethylene, the highest luminosity observed being in the case of a mixture consisting of 75 per cent. of ethylene and 25 per cent. of oxygen. On increasing the proportion of oxygen beyond this, the illuminating power of the mixture was again diminished, although the *intrinsic* luminosity of the ethylene was further increased. In the last experiment the proportion of oxygen mixed with the ethylene was sufficient to cause the individual jets of gas issuing from the separate apertures in the argand burner to become nearly isolated

ILLUMINATING POWER OF ETHYLENE WHEN BURNT WITH CARBONIC OXIDE & ATMOSPHERIC AIR RESPECTIVELY.

(EXPERIMENTAL LINES ONLY.)



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from their neighbours, the upper margin of the flame becoming frayed out into a number of tongues corresponding with the apertures in the burner.

Influence of Atmospheric Air as a Diluent.

Ethylene was also mixed with increasing proportions of atmospheric air, and the illuminating power of the mixtures determined. The following photometric observations were recorded:—

Percentage.		Candles observed.	Rate.		Candle-power corrected to 5 cubic feet of gas and 120 grains of spermaceti, per hour.
Ethylene.	Air.		Gas in cubic feet, per hour.	Candles in grains, per hour.	
79·68	20·32	28·36	2·53	116·7	54·45
67·15	32·85	29·82	3·10	112·5	45·84
55·92	44·08	26·49	3·68	123·8	37·16
42·69	57·31	30·71	5·12	107·2	26·78
33·91	66·09	20·86	6·16	115·0	16·22
22·31	77·69	1·00	8·20	120·0	0·61
13·31	86·69	explosive mixture.			

These results and the curves in the diagram show that the admixture of atmospheric air has less influence upon illuminating gas than either nitrogen or carbonic anhydride. The illuminating power of the mixtures becomes diminished as the proportion of air increases, the disillumination of the ethylene being effected by the same degree of dilution as in the case of nitrogen, viz., when the proportion of ethylene falls to about 22 per cent. of the mixture. On the other hand, the intrinsic luminosity of the ethylene undergoes no diminution until the air forms about 50 per cent. of the mixture. Indeed the admixture of air acts but very little more prejudicially upon the illuminating power than does the addition of carbonic oxide.

The same precautions were taken to avoid an explosive mixture as in the case of mixtures with oxygen. A mixture containing 22·31 per cent. of ethylene was found to be inflammable without explosion, whilst one containing only 13·31 per cent. was explosive.

The great superiority of atmospheric air over either nitrogen or carbonic anhydride as a diluent is further shown by the fact that whilst carbonic anhydride or nitrogen saturated with the vapour of benzene at the ordinary temperature of the air is non-inflammable, atmospheric air so saturated yields, as is well known, a light of some brilliancy.

Influence of Aqueous Vapour on the Illuminating Power of Ethylene and Coal-gas.

All the photometric determinations hitherto recorded in this and my previous paper were made with gas saturated with moisture at the temperature of the photometric room. In order to ascertain the influence which this moisture exerts upon the illuminating power of the gas, experiments were now made with dried and undried gas respectively. The gas, when burnt as it comes from the meter, is necessarily saturated with moisture; the dried gas, on the other hand, was obtained by interposing between the meter and the burner a wide tube closely packed with fused calcium chloride. In order to avoid any difference in the composition of the gas in the case of ethylene, half the holder was consumed undried and the other half dried. With ethylene, the following results were obtained:—

	Candles observed.	Rate.		Candle-power corrected to 5 cubic feet of gas and 120 grains of spermaceti, per hour.
		Gas in cubic feet, per hour.	Candles in grains, per hour.	
Dry ethylene	25·94	1·75	115·0	70·97
Moist „	26·92	1·97	116·5	66·25
Dry ethylene	27·26	1·87	116·3	70·64
Moist „	28·72	1·97	113·6	69·08
Dry ethylene	29·50	1·93	112·5	71·63
Moist „	25·46	1·81	120·0	70·40
Dry ethylene (average)..	..	..	..	71·08
Moist ethylene (average)	..	..	..	68·58

Thus the average of the three experiments shows that the presence of about 2 per cent. of aqueous vapour (the proportion present in gas saturated at 20° C. and 760 mm.) effects a reduction of between two and three candles, or 3·6 per cent. of the illuminating power of the ethylene.

Similar experiments were made with moist and dry coal-gas with the following results:—

	Candles observed.	Rate.		Candle-power corrected to 5 cubic feet of gas, and 120 grains of spermaceti, per hour.
		Gas in cubic feet, per hour.	Candles in grains, per hour.	
Dry coal-gas.....	20·14	4·82	101·7	17·69
Moist „	14·16	3·88	110·5	16·79
Dry coal-gas.....	20·94	5·39	106·9	17·32
Moist „	19·50	5·26	110·7	17·08
Dry coal-gas (average)..	..	..	..	17·50
Moist coal gas (average)	..	..	..	16·93

Thus the 2 per cent. of aqueous vapour present in the moist gas appears to reduce the illuminating power by about half a candle, or 3·3 per cent.

That the presence of aqueous vapour in gas should tend to reduce its illuminating power was to be anticipated, since this aqueous vapour has to be raised to the temperature of the flame by the heat produced in the combustion of the gas. Moreover, the aqueous vapour at the temperature of the flame is partially dissociated, which dissociation is attended with a large absorption of heat. Indeed, that moisture reduces the illuminating power of coal-gas has been known to gas managers for a considerable time, and some years ago the London gas referees found that dried gas had a superiority in illuminating power over ordinary gas to the extent of from 6 to 8 per cent. This difference is even in excess of that recorded above.

On comparing the curves constructed from the above results with those in the previous paper (p. 38 of this volume), it will be seen how entirely different is the influence of combustible and incombustible diluents upon illuminating gas. Thus on reference to the curves in the previous paper, it will be seen that although the illuminating power of mixtures of ethylene with either hydrogen, carbonic oxide, or marsh-gas is invariably less than that of pure ethylene, yet the "*intrinsic*" luminosity of the ethylene undergoes no diminution until the proportion of the diluent forms a very considerable fraction of the whole mixture; and in the case of ethylene mixed with marsh-gas, the intrinsic luminosity of the ethylene actually increases, and that with accelerated rapidity as the proportion of marsh-gas becomes greater.

In the case of the incombustible diluents, excepting pure oxygen and atmospheric air, on the other hand, not only is the illuminating

power of the mixtures inferior to that of the pure ethylene, but the intrinsic luminosity of the ethylene itself becomes at once diminished, and this diminution continues until the luminosity is completely destroyed. Of carbonic anhydride, nitrogen, aqueous vapour, and atmospheric air, carbonic anhydride exerts the most, and atmospheric air the least prejudicial effect; indeed, the influence of the latter is not even as great as that of the proportion of nitrogen which it contains. The inequality in the disilluminating effects of these several incombustible diluents receives an explanation partly in the difference between their specific heats, and partly in the dissociation or reduction which takes place in the case of carbonic anhydride and aqueous vapour, but which is absent in the case of nitrogen, oxygen, and atmospheric air. Thus the specific heats of these gases, as given by Clausius (*Annalen*, **118**, 118), are:—

Air	1·00	Specific heat of equal volumes under constant pressure. Air = 1.
Oxygen	1·01	
Nitrogen	1·00	
Carbonic anhydride ...	1·39	
Water vapour	1·26	

That oxygen differs essentially in its effect from the other diluents receives an obvious explanation in the fact that it greatly increases the temperature of the flame, permitting the combustion of the hydrocarbon with less admixture of inert nitrogen. Thus the mixture of ethylene with oxygen actually burns under more favourable circumstances than pure ethylene itself burning in air; for not only is the intrinsic luminosity of the ethylene increased, but the illuminating power of the mixture is greater than that of pure ethylene.

Rosetti (*Gazzetta*, **7**, 422) has determined the temperature of flames in which mixtures of coal-gas with air, nitrogen, and carbonic anhydride respectively were consumed from a Bunsen burner closed below.

The temperature of the hottest part of the flame was in each case recorded, the results being as follows:—

	Air.	Nitrogen.	Carbonic anhydride.
1 vol. gas to 1 vol.	—	1180°	1100°
1 „ „ 2 „	1260°	1150	880
1 „ „ 3 „	1116	1040	780

On comparing these figures with the diagram of curves, it will be seen how closely they harmonise with each other. For not only does the higher flame temperature of gas mixed with air agree with the greater illuminating power of such mixtures, but it will be seen that as the proportion of the diluents is increased, the difference between

the flame temperatures of air and nitrogen is diminished, whilst the difference between these and that of carbonic anhydride is increased. In like manner, the illuminating power curves of mixtures of ethylene with air and nitrogen respectively converge as the proportion of diluent increases, whilst the illuminating power curve of ethylene mixed with carbonic anhydride diverges more and more from the curves for nitrogen and air. Thus the difference in flame temperature between a mixture of equal volumes of coal-gas and nitrogen and a similar mixture of coal-gas and carbonic anhydride is, according to Rosetti, only 80°, and from the diagram the difference in illuminating power (substituting ethylene for coal-gas) is about 10 candles, whilst with double the volume of carbonic anhydride and nitrogen, the difference in flame temperature is no less than 270°; the illuminating power of the mixture containing carbonic anhydride is zero, whilst the nitrogen mixture gives a light of about 10 candles. Again, taking mixtures with air and nitrogen, when either of these forms half the mixture, the difference in flame temperature between the two is 110°, and the difference in illuminating power 14 candles, whilst in mixtures containing 75 per cent. of either air or nitrogen, the difference between the two flame temperatures is only 76°, and the difference in illuminating power only two candles.

It has been stated by Heumann (*Journ. of Gas Lighting*, 1877, vol. 29, 491) "that at least three different causes may, any one of them, effect disillumination, viz., *refrigeration*, *dilution*, and *oxidation of the combustible material*." When ethylene is mixed with hydrogen, carbonic oxide, or marsh-gas, there is disillumination by "*dilution*" only, and in my previous paper I have shown that the disillumination of the mixture proceeds nearly throughout without any diminution in the intrinsic luminosity of the ethylene.

On the other hand, when ethylene is mixed with carbonic anhydride or nitrogen, there is disillumination both by "*dilution*" and by "*refrigeration*," and in the case of air also by "*oxidation of the combustible material*." That the disillumination is chiefly due to "refrigeration" is apparent from the great difference in degree between the behaviour of nitrogen and carbonic anhydride as diluents, which difference is dependent only upon the difference between their specific heats and the absorption of heat by reduction to CO in the case of CO_2, for their diluting power is obviously the same. In these cases of "*refrigeration*" the disillumination of the mixture is accompanied by a corresponding diminution in the intrinsic luminosity of the hydrocarbon.

In the case of atmospheric air, the disillumination appears to be principally due to "*dilution*" and "*oxidation of the combustible material*," for, as already pointed out, the intrinsic luminosity of the

ethylene is not affected by the admixture of air until the latter amounts to 50 per cent. of the whole. Indeed, the temperature of the flame is in all probability increased by the admixture of air, for the Bunsen flame is generally supposed to possess a higher temperature than a luminous one, although I am not aware that this assumption rests upon any accurate experimental foundation. That "*refrigeration*," however, ultimately comes into play also is probable from the fact that complete disillumination is effected by the same proportion of air as of nitrogen.

In the case of oxygen mixed with ethylene, there is in the first instance what I propose to term *superillumination*, *i.e.*, an actual increase in the illuminating power obtained by the addition of a gas which is itself non-luminous. This superillumination would doubtless have been found to be followed by gradual disillumination, if the curve could have been further pursued without danger of explosion; indeed, the curve, as far as it was traced, had already taken the direction towards diminished illuminating power, although the intrinsic luminosity of the ethylene was still increasing. This disillumination must be entirely due to "*oxidation of the combustible material*" as long as the oxygen remains insufficient for the complete combustion of the ethylene.

The principal results arrived at by these experiments may be summed up as follows:—

1. Mixtures of ethylene with the combustible diluents, carbonic anhydride, nitrogen, aqueous vapour, and atmospheric air, possess a lower illuminating power than pure ethylene.

2. In all mixtures of ethylene with either carbonic anhydride, nitrogen, or aqueous vapour, the intrinsic luminosity of the ethylene is reduced.

3. In mixtures of ethylene with atmospheric air, the intrinsic luminosity of the ethylene remains unimpaired until the air forms about 50 per cent. of the mixture.

4. Mixtures of ethylene with oxygen in insufficient quantity to form an explosive mixture, possess a greater illuminating power than pure ethylene, the intrinsic luminosity of the ethylene being greatly increased.

5. The disilluminating effects of carbonic anhydride, nitrogen, and water-vapour are partly due to "dilution" and partly to "refrigeration," or the cooling occasioned by the introduction of inert gas into the flame; this refrigeration is proportional to the specific heats of the gases, but in the case of carbonic anhydride and aqueous vapour, it is also augmented by the absorption of heat which takes place in the dissociation of the aqueous vapour, and in the reduction of the carbonic anhydride to carbonic oxide.

6. Of the four diluents, carbonic anhydride, nitrogen, aqueous vapour, and atmospheric air, carbonic anhydride is the most and atmospheric air the least perjudicial to the illuminating power. Nitrogen and atmospheric air, however, become more equalised in their effect as the proportion in which they are present increases; complete disillumination of the ethylene being effected by the same proportion of each.

XXXVI.—*A New Form of Pyrometer.*

By Thos. Carnelley, D.Sc. (Lond.), and Thos. Burton, University College, Dundee.

It is a well-known fact that none of the pyrometers which have been proposed at various times for measuring high temperatures are of a sufficiently simple construction, or admit of such ready manipulation as to be extensively employed in the arts, whilst in those cases where these conditions are fulfilled, the results are not so exact or so constant as could be wished. Some, as the specific heat method, only allow of the temperature being determined at a particular moment, so that a continuous observation of a gradual rise in temperature is not possible, whereas in many cases this is the kind of observation required. Further, the use of most, if not all pyrometers, is limited to temperatures considerably below the fusing point of the material used in their construction. A simple and easily manipulated pyrometer, which can be used for the determination of temperatures no matter how high, and which at the same time admits of a gradual rise in temperature being observed, and is also sufficiently accurate and constant, is therefore a great desideratum for many manufacturing purposes.

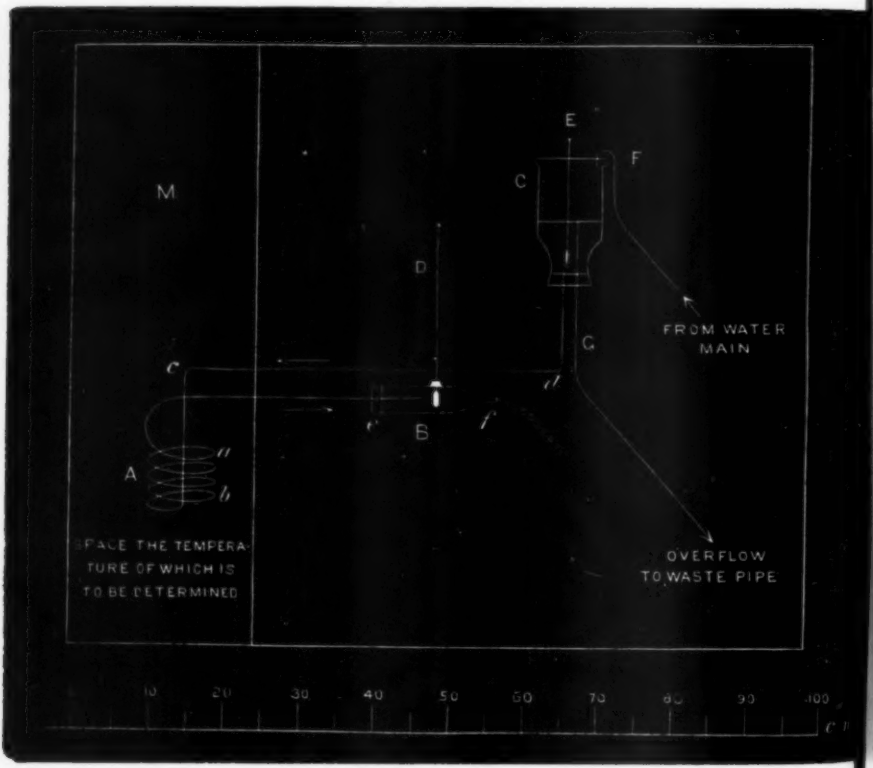
The instrument which we shall describe below was invented and used by one of us about four years ago, but pressure of other engagements prevented its capabilities being thoroughly tested until quite recently. Though it has several drawbacks, yet for many purposes it overcomes most of the difficulties attaching to the older pyrometers. Being extremely simple in its construction and arrangement, it is cheap, and does not readily get out of order; moreover, when once placed in position, it requires little or no manipulation except the reading off of a couple of thermometers and a reference to a table.

The principle of the method is as follows:—

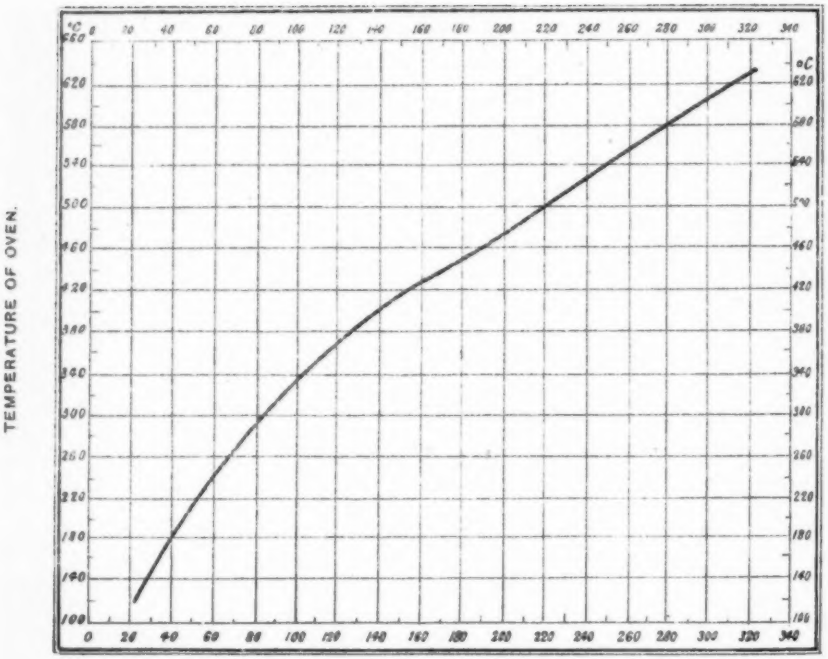
If a current of water of known temperature be allowed to flow at a constant rate through a coiled metallic tube placed in the space the

temperature of which is required, then the increase in the temperature of the outflowing water will be the greater, the higher the temperature of the space.

The form and method of using the new pyrometer will be readily understood from the attached sketch, which is drawn to scale, and is one-tenth of the actual size of the apparatus used in our experiments.



A is a coil of copper tubing placed in the space M, of which the temperature is required. A current of water flows from the cistern C, through the coil A, into the glass tube B, and out at the nozzle *f*. The tube F, attached to the water main, feeds the cistern at such a rate as to maintain a small but continual overflow through the tube G, which is connected with the waste-pipe. By this means a uniform head of water is obtained, so that the current flows through the coil at a constant rate. The effluent branch of the copper coil projects such a distance into the tube B that the issuing water flows directly on to the bulb of the thermometer D. The two thermometers E and



TEMPERATURE OF OVEN.

DIFFERENCES OF TEMPERATURE IN TENTHS OF DEGREES BETWEEN THE OUT AND IN-FLOWING WATER.

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D serve to determine the temperatures of the inflowing and outflowing water respectively. They are graduated to $\frac{1}{5}$° C., so that the temperature can be read off easily to $\frac{1}{10}$° C.

The copper tube has an internal diameter of 6 mm. The coil itself, which has five complete turns, is about 8 cm. high, and has an external diameter of 8 cm. The head of water in the cistern G, above the outflow *f*, was 20 cm. in our experiments, the average flow of water at a temperature of 80° C. being 813 c.c. per minute measured at a temperature of 10°.

For the purpose of graduation, the pyrometer was exposed in a cylindrical oven of sheet iron (23 cm. deep and 15 cm. diameter) heated in a small coke furnace. This oven was enclosed on all sides. To begin with, the oven was heated to the highest temperature attainable under the circumstances, and then allowed to cool down slowly. During the cooling process the temperature of the out- and in-flowing water was read off periodically, and the actual temperature of the oven estimated simultaneously by exposing therein metallic salts of known melting points (this Journal, **29**, 489, and **33**, 273, 281) enclosed in capillary tubes, or for temperatures below 300° an ordinary thermometer. From the results thus obtained, a series of curves was constructed showing the relation between the temperature of the oven and the increase in temperature of the effluent water. In the diagram is shown the mean curve deduced from a number of such experiments. The greatest deviation from this curve in any single instance, and for any temperature up to 650°, is within 25°*, the average error being 9°.

In a large furnace it is possible that this curve would become more nearly a straight line, for, in our case the oven being small in proportion to the size of the coil, we think there might be an appreciable cooling effect on the thermometer or on the metallic salts employed for comparison, since for a given increase in the temperature of the outflowing water, the temperature would be really higher than that indicated by the thermometer or salts, and this would be the more so the higher the real temperature of the oven. With our comparatively small oven, the thermometer and salts had necessarily to be placed too

* Even this is undoubtedly very much greater than would be the case in the actual circumstances in which the pyrometer would be used. For owing to our coil being large in proportion to the size of our oven, the thermometer or salts used for obtaining the real temperature were in much too close proximity to the coil, so that a small difference in their distance from it would, owing to the cooling effect of the coil, affect to a certain extent the reading of the thermometer or the fusion of the salts. The consequence would be, therefore, that even when the oven was at exactly the same temperature, the thermometer would give a small difference in reading in two experiments, whilst the temperature given by the pyrometer would be the same in both cases.

near to the coil, whereas in an ordinary furnace this would not be the case.

The real cause, however, of the divergence of the curve from a straight line is doubtless that the copper tube will be heated not only by contact with the hot gases, but also by radiation from the walls of the oven. This last process of heating will be more energetic when the difference of temperature between the walls of the oven and the tube is greater. For this reason, therefore, we should expect that the curve would be similar to that shown in the plate, the temperature of the water rising more rapidly as the temperature of the furnace increases.

From our experience of the instrument, we believe that under any given set of conditions the curve would admit of extension far beyond the limits of experiments made for calibrative purposes. But what we lay special stress on is, that when once placed in position in any given furnace, a certain increase in the temperature of the outflowing water will always indicate to the operator that a desired temperature has been reached, independently of any knowledge of what that particular temperature may be as measured on an ordinary thermometrical scale.

Each instrument, and every variation in the head of water, will of course require a distinct table. But when once one of these pyrometers is set in position in a furnace, with a constant head of water, one table will be all that is necessary. As, however, in most manufacturing operations the actual temperature in so many degrees, centigrade or Fahrenheit, is not necessarily required, it will be quite sufficient for the workman to know the increment in temperature of the outflowing water, and he would soon accustom himself to represent all the different states of the furnace in terms of this increment.

We do not claim for this form of pyrometer a scientific degree of accuracy, but we believe that in those cases in which its use is permissible, it will be found of great value, and sufficiently accurate for almost all purposes, especially in manufacturing operations where a measurement of high temperatures is required, and where an error of a few degrees is of little consequence.

By a proper choice in the bore and size of the coil, and rate of flow, this pyrometer can evidently be used for any temperature however high; but on the other hand it cannot be employed for ascertaining the actual temperature of liquids, unless, indeed, it has been graduated in the same medium. This is of course due to the fact that the instrument gives very different readings in two distinct liquids, even though the latter be at the same temperature, this difference depending chiefly on the difference of the specific heats of the two liquids.

The pyrometer is best adapted for determining the temperature of

a closed space filled with air, such as a muffle, oven, or kiln. But it may even be used for liquids, if it be borne in mind that a given graduation of the instrument holds for that particular liquid only in which it has been graduated. There are many cases in which it may be of service under these latter circumstances, as in the boiling of linseed oil for the manufacture of oil-cloth, the temperature of the oil ranging somewhat above that at which a mercury thermometer can be used. In this case it is necessary for the workman to have some means of knowing the degree of heat attained, for if the temperature rises above a certain point, the oil is very liable to boil over suddenly. One of the purposes for which we think the pyrometer will be most useful is for pottery kilns, for it would give much more accurate results, and with less trouble, than the method generally adopted, viz., the shrinkage of trial pieces of clay.

In conclusion we should say, that when we had almost completed our work we noticed a paper by Lauth (*Bull. Soc. Chim.*, **40**, 108) on a form of pyrometer recently devised by Messrs. Boulier Bros. The principle of this instrument is exactly identical with that of our own, and is said to be at present in use at the Sèvres porcelain manufactories. With regard to priority, we can only repeat that our pyrometer, both in principle and in form, was invented by one of us as long ago as 1879, with the special view of its use in the pottery manufactures. It was first used on a small scale in the laboratory in 1881.

XXXVII.—*Refraction-equivalents of Organic Compounds.*

By J. H. Gladstone, F.R.S.

On March 3, 1870, I had the honour of delivering a lecture before this Society "On Refraction-equivalents"; this was published in the Journal (*Chem. Soc. J.*, 1870, 101), and was immediately followed by a paper "On the Refraction-equivalents of the Aromatic Hydrocarbons and their Derivatives" (*ibid.*, 1870, 147). For nearly ten years very little progress was made with the subject, either in England or abroad. In a lecture at the Royal Institution in 1877, I had, however, given a more complete table of the refraction-equivalents of the elements, and entered more fully on the numerical relations that exist between these equivalents, as well as on the bearing of the subject upon the determination of the rational composition of organic bodies.

A series of papers by Brühl, commencing in November, 1879, again

called attention to the subject (*Annalen*, **200**, 139; **203**, 1, 255, and 363; *Wien. Akad. Ber.*, 1881, **11**, 84, 1). These papers, as far as they relate to refraction of light, proceed on the same lines as those of Landolt; they add largely to our store of good observations, and especially point out that there is a great increase of refraction, not only in the aromatic group, as was previously known, but wherever the carbon elements are supposed to be united by double bonds: so that he considers each carbon-atom in such a case to have the refraction-equivalent, not of 5·0, but of 6·1. He likewise came to the conclusion that oxygen has also two values, according to whether it is combined singly or doubly.

About the same time, several organic chemists recognised the assistance which this property gave them in their researches, and Dr. Thorpe showed the relation between the refractive power of substances and their specific volumes (*Chem. Soc. J.*, 1880, 327). Important papers have also recently appeared on the refraction of light by sulphur compounds by Nasini (*Gazzetta*, **13**, 226), and by Kanonnikoff on the relation between refractive power and chemical composition (*Journal Russian Physico-Chemical Society*, 1883, 434).

The deductions of Brühl led me, three years ago, to take up the matter afresh in relation to the refraction and dispersion of isomeric bodies, and especially to revise the evidence in regard to the refraction-equivalents of carbon, hydrogen, oxygen, and nitrogen in organic compounds, and to send my conclusions to the Royal Society (*Proc. Roy. Soc.*, 1881, 327). In that brief communication, I expressed a hope shortly to submit to the public the whole of my recent observations.

These observations have been made from time to time since 1870, and such of them as relate to organic compounds, and may be considered fairly trustworthy, are given in the subjoined tables. When they are substances which have been previously determined by me, as in the case of amylene, quinoline, or thymol, it is to be understood that I consider the present observations more correct; when they are substances which have been also determined by Brühl, Janovsky, or Kanonnikoff, they must be regarded simply as independent observations of different specimens.

I have to express my acknowledgments to the Committee of Council on Education for allowing me to examine the liquid substances exhibited by the German Chemical Society at the Loan Collection of Scientific Apparatus in 1876. They were diethylamine, triethylamine, formamide, xylidine, allylamine, allyl sulphide, and ethyl thiocyanate from Hofmann's laboratory: furfurol, nitroethane, capronitrile, and allylamine from Kahlbaum; mesitylene, monochlorotoluene, xylene, and styrolene from Trommsdorf; metacresol

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from Oppenheim; together with paraldehyde, propionitrile, butyl chloral, and isobutyl chloride. Professor Crum-Brown also kindly lent me at the same time his specimens of valero- and benzo-nitrile, methyl alcohol, bromacetic ether, and benzyl-phenyl-carbamide. I am also indebted to Dr. Mills for a collection of specimens of nitro-compounds of the aromatic series: to the late Dr. Stenhouse for erythrol; to Professor Armstrong for camphoric acid, $C_{10}H_{20}$ (prepared by the action of iodine on camphor), and sylvestrene; to Dr. Wright for his specimens of oxidised essential oils; to Dr. Hodgkinson for acetates of the aromatic series, benzylic isobutyrate, and an isomeric $C_{11}H_{14}O_2$, as well as for difluorene and diparafluorene; to Dr. Thorpe for picoline; to Dr. Perkin for coumarin, and a collection of compound ethers comprising three oxyphenyl acrylates, two citraconates, two mesaconates, two tetramethylene carbonic ethers, allyl acetoacetic ether, and allyl-malonic ether; to Professor Vernon Harcourt for pentane; to Messrs. Barnes and Company for pure specimens of benzene, toluene, aniline, and nitrobenzene; and to Mr. Levinstein for meta- and para-xylene. Many of the other substances were prepared or purified in my own laboratory.

The refractive indices deduced from the observations of the lines A, D, and H in the liquid bodies are given in Table I, together with the density. Where the absorption of the most refrangible rays was too great to admit of H being seen, the line F or D was measured instead, and that is indicated in the table by the insertion of one or other of those letters.

It was not thought desirable to give these figures for the solutions of solid bodies, as they would serve no purpose without the refraction of the particular specimen of the solvent employed in each case; but the nature of the solvent is indicated in Table II, together with the percentage amount of the substance dissolved; the strength of the solution is of importance as an element in estimating the trustworthiness of the result.

Table III gives the specific refraction, dispersion, and refraction-equivalent of all the substances in the preceding tables, deduced from the observations or from the mean of them where there are more than one. The specific refraction is the refractive index for the line A, minus unity, divided by the specific gravity $\frac{\mu_A - 1}{d}$. The specific dispersion is the difference between the specific refraction of the lines A and H, $\frac{\mu_H - 1}{d} - \frac{\mu_A - 1}{d}$, or, which is the same thing, $\frac{\mu_H - \mu_A}{d}$. The refraction-equivalent is the specific refraction for the line A multiplied by the atomic weight, $P\frac{\mu_A - 1}{d}$. The last column gives the theo-

retical refraction-equivalent calculated from the following values of the respective elements. The reasons for the adoption of these values will be subsequently explained.

Carbon, saturated	5·0
„ in C_nH_n	5·95
„ double linked	6·1
Hydrogen	1·3
Oxygen, joined by single bonds	2·8
„ joined by a double bond	3·4
Nitrogen	4·1
„ in bases, NO_2, &c.	5·1
Chlorine	9·9
Bromine	15·3
Iodine	24·5
Sulphur, joined by single bonds	14·1
„ joined by a double bond	16·0

The values are calculated according to the received theories as to the constitution of the bodies, the rational formulæ furnished by Perkin for his compound ethers, or what appeared to be indicated by the observations themselves. No calculation has been attempted for substances containing an excessive amount of carbon, or those which are manifestly anomalous.

TABLE I.—*Liquid Bodies.**

Substance.	Temp. C.	Density.	Refractive indices.		
			μ_A.	μ_D.	μ_H.
Hydrocarbons.					
Pentane	11·5°	0·624	1·3536	—	—
Amylene	21	0·6503	1·3712	1·3758	1·3907
Hexane, b.p. 48—52° C.	25·5	0·6317	1·3562	1·3602	1·3715
„ b.p. 53—60° C.	25	0·6413	1·3608	1·3648	1·3763
Benzene	10	0·8903	1·4978	1·5078	1·5411
„	10	0·8901	1·4981	1·5083	1·5416
„ (Barnes)	7·5	0·8881	1·4972	1·5070	1·5402
Toluene	7·5	0·8704	1·4895	1·4982	1·5297
Xylene	18	0·8632	1·4874	1·4966	1·5272
Metaxylene	15·5	0·8726	1·4932	1·5020	1·5335
Paraxylene	16	0·8488	1·4766	1·4846	1·5130
Styrolene (Trommsdorf)	11	0·9409	1·5208	1·5311	1·5693
„	—	0·9084	1·5040	1·5142	1·5489

* Where more observations than one are given, it is to be understood that they are in nearly all cases different specimens.

Substance.	Temp. C.	Density.	Refractive indices.		
			μ_A.	μ_D.	μ_H.
Mesitylene	19°	0·8632	1·4855	1·4960	1·5257
Cumene	12	0·8432	1·4725	1·4801	1·5064
$C_{10}H_{20}$	12	0·8046	1·4369	1·4417	1·4567
Sylvestrene	14	0·8658	1·4712	1·4779	1·4987
Nutmeg oil, b.p. 163—164° C.	25	0·8454	1·4594	1·4655	1·4859
„ b.p. 177—179° C.	27	0·8480	1·4667	1·4742	1·4973
Hesperidene	—	0·8483	1·4677	1·4741	1·4954
Cedrene	18	0·9231	1·4964	1·5028	1·5240
Halogen Compounds.					
Methylene diiodide	19	3·3188	1·7215	1·7421	1·8034
„	15·5	3·326	1·7218	1·7419	—
„	15	3·328	1·7232	1·7435	F1·7705
Ethylene chloride	14	1·272	1·4437	1·4485	1·4647
Ethylidene chloride	—	1·201	1·4190	1·4237	1·4380
Ethyl iodide	14	1·9313	1·5067	1·5164	1·5480
Propylene dibromide	18	1·8893	1·5084	1·5162	1·5405
„	21	1·910	1·5101	1·5177	1·5423
Propyl iodide	16	1·7508	1·4979	1·5069	1·5359
Isopropyl iodide	14	1·7157	1·4947	1·5040	—
Allyl bromide	24·5	1·3867	1·4536	1·4613	1·4870
„	20·5	1·396	1·4565	1·4620	1·4894
Isobutyl chloride	19	0·8626	1·3939	1·3979	1·4111
Isobutyl iodide	—	1·5982	1·4874	1·4952	1·5240
Amylene bromide	21°	1·656	1·5006	1·5076	1·5304
Amyl iodide	14	1·5048	1·4884	1·4960	1·5215
Secondary amyl iodide	—	1·4792	1·4885	1·4970	1·5255
Secondary hexyl iodide	—	1·4193	1·4870	1·4948	1·5192
Monobromobenzene	23	1·49225	1·5476	1·5586	1·5971
„	16	1·4958	1·5502	1·5610	1·5995
Benzyl chloride	7	1·099	1·5314	1·5415	1·5764
Chlorotoluene	19	1·0761	1·5173	1·5271	1·5613
Orthobromotoluene	—	1·4192	1·5502	1·5608	1·5981
Naphthalene dichloride	12·5	1·287	1·6122	1·6272	F1·6476?
„	18	1·2648	1·6096	1·6247	—
Monobromonaphthalene	17	1·5403	1·6471	1·6647	1·7369
„	16·5	1·5678	1·6491	1·6669	1·7394
„	18	1·5403	1·6456	1·6630	1·7352
Oxygen Compounds.					
Methyl alcohol	18	0·7961	1·3270	1·3301	1·3399
Ethylene alcohol	22·5	1·112	1·4261	1·4306	1·4440
Allyl alcohol	23	0·8563	1·4054	1·4111	1·4289
Isobutyl alcohol	20·5	0·8024	1·3914	1·3956	1·4083
Phenol	21	1·0598	1·5394	1·5509	1·5898
Cresol	23	1·039	1·5316	1·5419	1·5787
Metacresol	19	1·0330	1·5259	1·5364	1·5726
Benzyl alcohol	22	1·0412	1·5278	1·5370	1·5710
Cinnamic alcohol	13	1·0318	1·5465	1·5579	1·6022
Butyl chloral	7	1·4111	1·4798	1·4858	1·5049
Valeral	25	0·8061	1·3856	1·3902	1·4034
Furfuraldehyde	19	1·1344	1·5002	1·5137	F1·5319
Paraldehyde	19	0·9909	1·3976	1·4017	1·4137

Substance.	Temp. C.	Density.	Refractive indices.		
			μ_A.	μ_D.	μ_H.
Mesityl oxide	19°	0·8528	1·4298	1·4371	1·4615
Cajeputol	21·5	0·9207	1·4546	1·4594	1·4758
Citronellol	—	0·890	1·4607	1·4667	1·4860
Absinthol	22	0·9128	1·4461	1·4508	1·4675
Cuminic aldehyde	20	0·9775	1·5186	1·5301	1·5718
Phenyl ether	24	1·0744	1·5702	1·5826	1·6286
„	25	1·0712	1·5675	1·5803	1·6258
Cresyl ether	16	1·0352	1·5576	1·5700	F1·5851
Eugenic acid	17·5	1·066	1·5288	1·5390	F1·5523
Ethyl bromacetate	18	1·5250	1·4494	1·4552	1·4712?
Allyl acetate	24·5	0·9258	1·4015	1·4065	1·4200
Benzyl acetate	21	1·0400	1·5150	1·5242	1·5491
„	22·5	1·03814	1·5134	1·5227	1·5543
Cresyl acetate	23	1·0499	1·4910	1·4991	1·5276
Acetyltetramethylene-carboxylic ether	13	1·0668	1·4743	1·4818	1·5078
Allylacetoacetic ether	13·5	0·9938	1·4356	1·4410	1·4593
Phenylethyl acetate	22·5	1·0507	1·5019	1·5108	F1·5218
Cinnamene acetate	22	0·9416	1·4880	1·4964	1·5240
Benzyl isobutyrate	23	1·0058	1·4833	1·4910	1·5166
$C_{11}H_{14}O_2$	22	1·0228	1·4886	1·4963	1·5226
Methyl citraconate	15·5	1·1164	1·4442	1·4504	1·4721
Methyl mesaconate	16	1·1246	1·4992	1·4564	1·4813
Ethyl citraconate	16·5	1·048	1·4397	1·4459	1·4659
Ethyl mesaconate	16	1·050	1·4433	1·4499	1·4727
Allyl-malonic ether	14	1·01475	1·4287	1·4338	1·4499
Tetramethylene dicarbonic ether	14	1·0484	1·4310	1·4369	1·4519
α-Methylorthoxyphenylacrylate of methyl	8·5	1·1465	1·5577	1·5727	1·6428
β-Methylorthoxyphenylacrylate of ethyl	9·5	1·1556	1·5722	1·5912	1·6860?
Ethylorthoxyphenylacrylate of ethyl	10	1·090	1·5438	1·5579	1·6298
Nitrogen Compounds.					
Diethylamine	19	0·7092	1·3824	1·3871	1·4015
Triethylamine	19	0·7317	1·3957	1·4005	1·4157
Allylamine (Hofmann)	19	0·7684	1·4138	1·4200	1·4402
„ (Kahlbaum)	11	0·7775	1·4198	1·4260	1·4509
„	17·5	0·7693	1·4166	1·4228	1·4433
„	10·5	0·7754	1·4207	1·4272	1·4475
Propionitrile	19	0·7862	1·3645	1·3681	1·3795
Valeronitrile	18	0·8010	1·3872	1·3917	1·4042
Capronitrile	18	0·8040	1·4044	1·4087	1·4223
Benzonitrile	18	1·0052	1·5195	1·5306	1·5699
Pyrroline	—	0·9606	1·4987	1·5074	1·5380
Picoline	23·5	0·94093	1·4912	1·5006	1·5317
Aniline	13	1·016	1·5695	1·5828	1·6336
„ (Barnes)	7·5	1·0322	1·5780	1·5921	1·6449
Xylidine	19	0·9867	1·5467	1·5585	F1·5741
Quinoline	10	1·1021	1·6158	1·6330	1·7012
„	10	1·096	1·6101	1·6282	F1·6504
Formamide	19	1·1462	1·4425	1·4493	1·4712

Substance.	Temp. C.	Density.	Refractive indices.		
			μ_A.	μ_D.	μ_H.
Benzyl-phenyl-carbamide.....	18°	0·9168	1·4950	1·5039	1·5349
Bromopicrin	13	2·816	1·5736	1·5831	—
Nitroethane	18	1·0550	1·3889	1·3934	1·4095
Ethyl nitrate	25	1·1067	1·3780	1·3826	1·3976
Amyl nitrite	21	0·8734	1·3967	1·4013	1·4162
Nitrobenzene	7·5	1·2121	1·5441	1·5580	F1·5767
Nitrotoluene	15·5	1·1649	1·5376	1·5509	F1·5695
Sulphur Compounds.					
Allyl sulphide	11	0·8544	1·4531	1·4598	1·4811
Ethylthiocarbimide	18	1·0030	1·5040	1·5142	1·5477

TABLE II.—*Solutions.*

Substance.	Solvent.	Percentage of substance.	
Hydrocarbons.			
Naphthalene	Benzene	18·53	16·66
,, ...	Ether	17·86	
,, ...	Carbon bisulphide	16·36	
Diphenyl.....	Benzene	33·33	
Dibenzene	,, ...	21·13	
Stilbene	,, ...	9·57	8·29
Phenanthrene	Carbon bisulphide	8·25	14·28
Pyrene	,, ...	15·82	
,, ...	Benzene	9·14	
,, ...	Chloroform	11·5	
Diparafluorene	,, ...	20·91	
Difluorene	,, ...	3·88	
Halogen.			
Dichloronaphthalene	Alcohol	9·63	
Oxygen Compounds.			
Erythrol.....	Water	10·03	
Mannitol	,, ...	12·06	15·38
Resorcinol	,, ...	39·18	
Thymol	Alcohol	69·75	67·06
Naphthol	,, ...	17·77	
,, ...	Ether	31·47	
Coumarin	Alcohol	4·65	
,, ...	Oil of Anise	26·36	
Lactic acid	Water	78·67	
Pyrogallol	,, ...	9·36	
Phthalic acid	Alcohol		
Cinnamic acid	,, ...	10·12	
Camphoric acid (Armstrong) ..	,, ...	17·65	17·11
,, ...	,, ...	21·68	33·89

Substance.	Solvent.	Percentage of substance.		
Nitrogen Compounds.				
Methylamine	Water	29·35		
Ethylamine	„	30·32		
Naphthylamine	Alcohol	14·77		
Ammonium carbamate	Water	25·58		
Ammonium anisate	„	5·35		
Alloxan	„	13·06		
Nitromannitol	Ether	4·97		
Dinitrobenzene	Nitrobenzene	18·27		
„	Benzene	12·24		
Nitraniline, *α*-	„	1·24		
„	Alcohol	3·48	4·23	
Nitraniline, *β*-	„	3·40	2·6	3·39
Trinitrotoluene	Benzene	5·11	8·71	
Nitrobenzoic acid, *α*-	Aqueous potash	5·48		
Nitrobenzoic acid, *β*-	„	5·68		

TABLE III.—*Mean Results of Observations on all Substances.*

Substance.	Molecular composition.	Specific refraction.	Specific dispersion.	Refraction-equivalent A.	
				Observed.	Calculated.
Pentane	C_5H_{12}	0·5667	—	40·80	**40·6**
Amylene	C_5H_{10}	0·5708	0·0300	39·95	40·2
Hexane, b.p. 48—52° C.	C_6H_{14}	0·5638	0·0243	48·49	48·2
„ b.p. 53—60° C.	C_6H_{14}	0·5626	0·0242	48·38	48·2
Benzene	C_6H_6	0·5595	0·0486	43·64	43·5
Toluene	C_7H_8	0·5624	0·0462	51·74	52·0
Xylene	C_8H_{10}	0·5646	0·0461	59·85	**59·6**
Metaxylene	C_8H_{10}	0·5652	0·0462	59·91	**59·6**
Paraxylene	C_8H_{10}	0·5615	0·0429	59·52	**59·6**
Styrolene	C_8H_8	0·5541	0·0505	57·62	58·0
Mesitylene	C_9H_{12}	0·5624	0·0466	67·49	67·2
Cumene	C_9H_{12}	0·5603	0·0403	67·23	67·2
$C_{10}H_{20}$	$C_{10}H_{20}$	0·5430	0·0246	76·02	76·0
Sylvestrene	$C_{10}H_{16}$	0·5442	0·0318	74·02	**73·0**
Nutmeg oil, b.p. 163—4° C.	$C_{10}H_{16}$	0·5438	0·0309	73·96	73·0
„ b.p. 177—9° C.	$C_{10}H_{16}$	0·5503	0·0360	74·84	75·2
Hesperidene	$C_{10}H_{16}$	0·5513	0·0327	74·98	75·2
Naphthalene	$C_{10}H_8$	0·5870	0·0782	75·14	—
Diphenyl	$C_{12}H_{10}$	0·5823	0·0724	89·68	—
Dibenzene	$C_{14}H_{14}$	0·5580	0·0440?	101·55	**101·5**
Stilbene	$C_{14}H_{12}$	0·6295	0·1452	113·39	—
Phenanthrene	$C_{14}H_{10}$	0·6085	F. 0·0456	108·31	—
Cedrene	$C_{15}H_{24}$	0·5377	0·0299	109·69	—
Pyrene	$C_{16}H_{10}$	0·6242	F. 0·0679	126·10	—
Diparafluorene	$C_{13}H_{10}$	0·5873	F. 0·0425	97·49	—
Difluorene	$C_{26}H_{18}$	0·6057	0·1108	199·87	—
Methylene diiodide	CH_2I_2	0·2172	F. 0·0185	58·22	—

Substance.	Molecular composition.	Specific refraction.	Specific dispersion.	Refraction-equivalent A.	
				Observed.	Calculated.
Ethylene chloride	$C_2H_4Cl_2$	0·3488	0·0165	34·53	—
Ethylidine chloride	$C_2H_4Cl_2$	0·3485	0·0162	34·50	35·0
Ethyl iodide	C_2H_5I	0·2623	0·0214	40·93	41·0
Propylene dibromide	$C_3H_6Br_2$	0·2681	0·0169	54·15	53·4
Propyl iodide	C_3H_7I	0·2844	0·0217	48·35	48·6
Isopropyl iodide	C_3H_7I	0·2883	D. 0·0054	49·02	48·6
Allyl bromide	C_3H_5Br	0·3271	0·0238	39·58	39·0
Isobutyl chloride	C_4H_9Cl	0·4566	0·0200	42·24	41·6
Isobutyl iodide	C_4H_9I	0·3050	0·0228	56·12	56·2
Amylene bromide	$C_5H_{10}Br_2$	0·3023	0·0180	69·53	68·6
Amyl iodide	$C_5H_{11}I$	0·3245	0·0220	64·26	63·8
Secondary amyl iodide	$C_5H_{11}I$	0·3302	0·0250	65·38	63·8
Secondary hexyl iodide	$C_6H_{13}I$	0·3432	0·0226	72·76	71·4
Monobromobenzene	C_6H_5Br	0·3674	0·0330	57·68	57·5
Benzyl chloride	C_7H_7Cl	0·4836	0·0409	61·02	60·6
Chlorotoluene	C_7H_7Cl	0·4807	0·0409	60·81	60·6
Orthobromotoluene	C_7H_7Br	0·3877	0·0337	66·29	66·0
Naphthalene dichloride	$C_{10}H_8Cl_2$	0·4778	F. 0·0275	95·28	—
Dichloronaphthalene	$C_{10}H_6Cl_2$	0·4766	0·0654	93·89	—
Monobromonaphthalene	$C_{10}H_7Br$	0·4177	0·0580	86·47	—
Methyl alcohol	CH_4O	0·4107	0·0162	13·14	13·0
Ethylene alcohol	$C_2H_6O_2$	0·3832	0·0161	23·75	23·4
Allyl alcohol	C_3H_6O	0·4734	0·0275	27·45	27·8
Isobutyl alcohol	$C_4H_{10}O$	0·4878	0·0209	36·10	35·8
Erythrol	$C_4H_{10}O_4$	0·3700	0·0184	45·14	44·2
Mannitol	$C_6H_{14}O_6$	0·3643	0·0140	66·32	65·0
Resorcinol	$C_6H_6O_2$	0·4591	0·0428	50·50	49·7
Phenol	C_6H_6O	0·5090	0·0476	47·84	47·2
Cresol	C_7H_8O	0·5116	0·0454	55·25	54·8
Metacresol	C_7H_8O	0·5091	0·0452	54·98	54·8
Benzyl alcohol	C_7H_8O	0·5069	0·0415	54·75	54·8
Cinnamic alcohol	$C_9H_{10}O$	0·5296	0·0540	70·96	69·6
Thymol	$C_{10}H_{14}O$	0·5262	0·0424	78·92	77·6
Naphthol	$C_{10}H_8O$	0·5487	0·0832	79·01	—
Butyl chloral	$C_4H_5Cl_3O$	0·3400	0·0178	59·67	59·6
Valeral	$C_5H_{10}O$	0·4783	0·0221	41·13	41·4
Furfuraldehyde	$C_5H_4O_2$	0·4409	F. 0·0280	42·33	—
Paraldehyde	$C_6H_{12}O_3$	0·4012	0·0163	52·95	54·0
Mesityl oxide	$C_6H_{10}O$	0·5039	0·0372	49·39	48·6
Coumarin	$C_9H_6O_2$	0·4846	0·0791	70·75	—
Cajeputol	$C_{10}H_{18}O$	0·4938	0·0229	76·04	76·8
Citronellol	$C_{10}H_{18}O$	0·5176	0·0284	79·71	79·0
Absinthol	$C_{10}H_{16}O$	0·4887	0·0234	74·28	74·2
Cuminic aldehyde	$C_{10}H_{12}O$	0·5305	0·0545	78·51	75·6
Phenyl ether	$C_{12}H_{10}O$	0·5302	0·0544	90·13	89·6
Cresyl ether	$C_{14}H_{14}O$	0·5386	F. 0·0266	106·64	104·8
Lactic acid	$C_3H_6O_3$	0·3566	0·0161	32·09	31·8
Pyrogallol	$C_6H_6O_3$	0·4740	D. 0·0076	59·72	—
Cinnamic acid	$C_9H_8O_2$	0·5205	0·0898	77·04	—
Camphoric acid	$C_{10}H_{16}O_4$	0·4040	0·0181	80·79	84·2
Eugenic acid	$C_{10}H_{12}O_2$	0·4961	F. 0·0220	81·36	—
Ethyl bromacetate	$C_4H_7BrO_2$	0·2947	0·0143	49·21	50·6
Allyl acetate	$C_5H_8O_2$	0·4336	0·0200	43·36	43·8

University of Michigan

Substance.	Molecular composition.	Specific refraction.	Specific dispersion.	Refraction-equivalent A.	
				Observed.	Calculated.
Benzyl acetate	$C_9H_{10}O_2$	0·4948	0·0361	74·22	—
Cresyl acetate	$C_9H_{10}O_2$	0·4677	0·0348	70·15	70·8
Acetyltetramethylene-carboxylic ether	$C_9H_{14}O_3$	0·4446	0·0314	75·58	72·8
Allylacetoacetic ether	$C_9H_{14}O_3$	0·4383	0·0210	74·51	75·0
Phenylethyl acetate	$C_{10}H_{12}O_2$	0·4776	F. 0·0190	78·34	78·4
Cinnamene acetate	$C_{10}H_{12}O_2$	0·5183	0·0382	84·99	—
Benzyl isobutyrate	$C_{11}H_{14}O_2$	0·4805	0·0331	85·53	86·0
$C_{11}H_{14}O_2$	$C_{11}H_{14}O_2$	0·4777	0·0332	85·03	86·0
Methyl citraconate	$C_7H_{10}O_4$	0·3979	0·0250	62·87	62·6
Methyl mesaconate	$C_7H_{10}O_4$	0·3994	0·0286	63·10	62·6
Ethyl citraconate	$C_9H_{14}O_4$	0·4196	0·0250	78·04	77·8
Ethyl mesaconate	$C_9H_{14}O_4$	0·4222	0·0280	78·53	77·8
Allyl-malonic ether	$C_{10}H_{16}O_4$	0·4225	0·0209	84·50	85·4
Tetramethylene-dicarbonic ether	$C_{10}H_{16}O_4$	0·4111	0·0199	82·22	83·2
α-Methylorthoxyphenyl-acrylate of methyl	$C_{11}H_{12}O_3$	0·4864	0·0734	93·39	88·4
β-Methylorthoxyphenyl-acrylate of methyl	$C_{11}H_{12}O_3$	0·4952	0·0984?	95·08	88·4
Ethylorthoxyphenylacrylate of ethyl	$C_{13}H_{16}O_3$	0·4989	0·0789	109·76	103·6
Methylamine	CH_5N	0·5471	0·0271	16·96	16·6
Ethylamine	C_2H_7N	0·5438	0·0264	24·47	24·2
Diethylamine	$C_4H_{11}N$	0·5392	0·0269	39·36	39·4
Triethylamine	$C_6H_{15}N$	0·5408	0·0273	54·62	54·6
Allylamine	C_3H_7N	0·5406	0·0359	30·81	31·4
Propionitrile	C_3H_5N	0·4636	0·0190	25·50	25·6
Valeronitrile	C_5H_9N	0·4833	0·0213	40·11	40·8
Capronitrile	$C_6H_{11}N$	0·5030	0·0222	48·79	48·4
Benzonitrile	C_7H_5N	0·5162	0·0501	53·17	52·2
Pyrroline	C_4H_5N	0·5191	0·0411	34·78	35·0
Picoline	C_6H_7N	0·5220	0·0431	48·54	48·6
Aniline	C_6H_7N	0·5601	0·0641	52·09	50·8
Xylidine	$C_8H_{11}N$	0·5540	F. 0·0278	67·05	66·0
Quinoline	C_9N_7N	0·5577	0·0785	71·94	—
Naphthylamine	$C_{10}H_9N$	0·5850	D. 0·0135	83·65	—
Formamide	CH_3NO	0·3860	0·0251	17·37	17·4
Ammonium carbonate	$CH_6N_2O_2$	0·3700	0·0210	28·86	28·9
Ammonium anisate	$C_9H_{11}NO_3$	0·4248	D. 0·0219	71·8	75·0
Benzyl-phenyl-carbamide	$C_{14}H_{16}N_2O$	0·5399	0·0435	123·10	120·6
Bromopicrin	CBr_3NO_2	0·2037	D. 0·0034	60·71	—
Nitroethane	$C_2H_5NO_2$	0·3686	0·0195	27·64	28·4
Ethyl nitrate	$C_2H_5NO_3$	0·3415	0·0178	31·07	31·2
Alloxan	$C_4H_2N_2O_4$	0·3239	0·0244	46·00	46·4
Amyl nitrite	$C_5H_{11}NO_2$	0·4542	0·0223	53·14	51·2
Nitromannitol	$C_6H_8N_6O_{18}$	0·2857	0·0161	129·14	128·6
Nitrobenzene	$C_6H_5NO_2$	0·4489	F. 0·0269	55·21	55·0
Dinitrobenzene	$C_6H_4N_2O_4$	0·3933	D. 0·0106	66·08	65·6
Nitraniline, α-	$C_6H_6N_2O_2$	0·4601	D. 0·0268	63·5	62·1
„ β-	$C_6H_6N_2O_2$	0·5464	D. 0·0311	75·4	—
Nitrotoluene	$C_7H_7NO_2$	0·4615	F. 0·0274	63·22	62·6
Trinitrotoluene	$C_7H_5N_3O_6$	0·3888	D. 0·0143	88·25	83·8

Substance.	Molecular composition.	Specific refraction.	Specific dispersion.	Refraction-equivalent A.	
				Observed.	Calculated.
Nitrobenzoic acid, *a*-.....	$C_7H_5NO_4$	0·3994	0·0388	66·70	66·2
" *β*-.....	$C_7H_5NO_4$	0·4004	0·0437	66·88	66·2
Allyl sulphide.....	$C_6H_{10}S$	0·5303	0·0327	60·45	59·3
Ethylthiocarbimide	C_3H_5NS	0·5025	0·0435	43·72	41·6

I have not included in the above table the refraction-equivalent calculated for the theoretical limit of the spectrum: the fact is that the doubts which Mr. Dale and I expressed in 1863 as to the position of this limit have been more than corroborated by the recent researches of Captain Abney and Professor Langley in the infra-red region. They have shown that rays capable of producing heat exist far beyond the theoretical limit as usually calculated. In the *Philosophical Magazine* for last March, there is the abridgement of a yet unpublished memoir by Langley, in which he investigates the whole subject and draws the following conclusions:—That "Cauchy's formula gives grossly erroneous results when extended far beyond the limits within which the observations on which it is founded are made." "That Briot's formula, though not exact, yet gives results much more trustworthy," and adds, as the result of his observations, that for the glass prism employed, "the deviation tends to become proportional to the wave-lengths as the deviation diminishes," and that "there is scarcely any limit to the wave-length the prism can transmit except that fixed by its absorptive effect." Under these circumstances it would appear of little use to calculate a supposed limit by any extrapolation formula.

Refraction-equivalents of the Elements.

I. *Carbon and Hydrogen.*

It was one of the first deductions of Landolt that the refraction-equivalent of the increment CH_2 is 7·6; and the whole progress of our knowledge since that time has only served to show that this figure is correct to one place of decimals. A large number of comparisons made in various ways have given me the mean value 7·63. But how much of this is due to carbon, and how much to hydrogen? Landolt, from a variety of considerations, concluded that the value of carbon was 5·0, and that of hydrogen 1·3. These figures were accepted by me, by Haagen, by Brühl, and others who worked upon the subject,

and they stand well the test of subsequent observations, including those which are here published. Some additional means of determination are also afforded by the above tables. Thus:—

Pentane	C_5H_{12}	=	40·80
	$5(CH_2)$	=	38·15
	2H	=	2·65

and

Hexane	C_6H_{14}	=	48·43
	$6(CH_2)$	=	45·78
	2H	=	2·65

The methyl alcohol in the above list was said to be extremely pure. We have the means of comparing it with other alcoholic bodies containing the same proportion of carbon and oxygen, but a larger proportion of hydrogen. Thus:—

2 Methyl alcohol =	$C_2H_8O_2$	=	26·28
Ethylene alcohol =	$C_2H_6O_2$	=	23·75
	2H	=	2·53
4 Methyl alcohol =	$C_4H_{16}O_4$	=	52·56
Erythrol =	$C_4H_{10}O_4$	=	45·14
	6H	=	7·42

and

6 Methyl alcohol =	$C_6H_{24}O_6$	=	78·84
Mannitol =	$C_6H_{14}O_6$	=	66·32
	10H	=	12·52

These calculations simply confirm the view that the refraction-equivalent of hydrogen must be very close to 1·3, and that consequently carbon must have a refraction-equivalent close to 5·0.

Higher Values of Carbon.

It was amongst the earliest of observations that certain organic compounds have a much higher refraction than could be accounted for on the supposition that carbon equals 5·0. It was shown, as far back as 1870, that in the whole of the aromatic group the refraction-equivalent was 6 or 7 above the calculated, and that the terpenes and many other substances, which have a large proportion of carbon, were also abnormally refractive. Brühl has confirmed and extended these observations, and by an elaborate and careful investigation has shown

that wherever there are carbon-atoms joined by double bonds, the refraction of each carbon may be estimated at 6·15 for the red line of hydrogen (the solar line C), or 5·86 for the limit of the spectrum calculated from Cauchy's formula.

While, however, Brühl's general conclusion appears to be fully established, the above figures are not quite compatible either with his own or with my observations on the simplest bodies of this character. I refer especially to the hydrocarbons of the formula C_nH_n.

From the table it will be seen that :—

Benzene,	C_6C_6,	has a refraction-equivalent for A of	43·66
Styrolene,	C_8H_8,	„ „ „	57·62
Dibenzyl,	$C_{14}H_{14}$,	„ „ „	101·55

hence—

in benzene each CH	= 7·27,	and each C	= 5·97
„ styrolene „	= 7·20,	„	= 5·90
„ dibenzyl „	= 7·25,	„	= 5·95

This low value is confirmed by the refraction of the chlorine and bromine substitution-products of benzene :—

Monochlorobenzene,	C_6H_5Cl,	has a refraction-equivalent of	52·1
Trichlorobenzene,	$C_6H_3Cl_3$,	„ „	69·7
Monobromobenzene,	C_6H_5Br,	„ „	57·75

hence—

in monochlorobenzene, each C	= 5·95
„ trichlorobenzene, „	= 6·01
„ monobromobenzene „	= 5·99

The refraction-equivalent of carbon for the line A appears therefore to be rather less than 6·0 in these multiples of CH.

But when we pass on to the higher members of the C_nH_{2n-6}-group, we find a higher value for the nucleus, C_6H_6 :—

Toluene,	C_6H_6, CH_2,	has a refraction-equivalent of	51·74
Xylene,	C_6H_6,$2CH_2$,	„ „	59·85
Cumene,	C_6H_6,$3CH_2$,	„ „	67·23
Mesitylene,	C_6H_6,$3CH_2$,	„ „	67·49
Cymene,	C_6H_6,$4CH_2$,	„ „	75·0

hence—

in benzene,	C_6H_6 = 43·66	and C	= 5·97
„ toluene	„ = 44·11	„	= 6·05
„ xylene	„ = 44·59	„	= 6·13
„ cumene	„ = 44·34	„	= 6·09
„ mesitylene	„ = 44·60	„	= 6·13
„ cymene	„ = 44·48	„	= 6·11

Hence it would appear that the introduction of only one CH_2 causes an elevation of the refractive power of the nucleus, though the increased refraction in toluene is not equal to that of the higher members of the series, when more atoms of carbon are introduced into the "side-chains."

Brühl's determination of toluene is practically identical with my own; but it is only fair to point out that the halogen compounds of toluene do not support the view of an intermediate value for six of the carbons in this body. They, and all the well-defined compounds of the aromatic series containing halogens or oxygen in the above table, confirm the value of about 6·1 for each double-linked carbon.

Benzyl chloride,	C_7H_7Cl	= 61·02, and C″	= 6·17
Chlorotoluene,	C_7H_7Cl	= 60·81, „	= 6·13
Bromotoluene,	C_7H_7Br	= 66·29, „	= 6·15
Resorcinol,	$C_6H_6O_2$	= 50·50, „	= 6·18
Phenol,	C_6H_6O	= 47·84, „	= 6·17
Cresol,	C_7H_8O	= 55·25, „	= 6·16
Metacresol,	C_7H_8O	= 54·98, „	= 6·11
Benzyl alcohol,	C_7H_8O	= 54·75, „	= 6·06
Thymol,	$C_{10}H_{14}O$	= 78·92, „	= 6·32
Phenylethyl acetate,	$C_{10}H_{12}O_2$	= 78·34, „	= 6·11
Cresyl acetate,	$C_9H_{10}O_2$	= 70·15, „	= 6·06
Benzyl isobutyrate,	$C_{11}H_{14}O_2$	= 85·53, „	= 6·05
Phenylic ether,	$C_{12}H_{10}O$	= 90·05, „	= 6·17
Cresylic ether,	$C_{14}H_{14}O$	=106·64, „	= 6·25

The two last bodies give a very great dispersion; hence the refraction for any particular ray will be more than usually affected by it. The whole list indicates a value a little above 6·1. We may therefore accept this as a very near expression of the refraction-equivalent for A of carbon when in that condition which is usually expressed by double linking, unless it be in the simplest combinations, when the evidence before us would make it about 0·15 less.

It is worthy of consideration whether this slight difference may not be due to some cause connected with the mode of experimenting. Two possible explanations suggest themselves. Thus, when we determine the refraction-equivalent for A, or for any other part of the visible spectrum, the coefficient of dispersion must enter into the result. Now double-linked carbon is very dispersive. But as the length of the spectrum of the hydrocarbons of the C_nH_{2n-6} series does not differ widely—and in fact benzene is rather the longest—the values deduced for any less refrangible ray will not be brought nearer together. The following is the value for double-linked carbon for the supposed limit as calculated by Brühl:—

Benzene, 42·16, C″= 5·74
Toluene, 50·06, „ = 5·81
Mesitylene, 65·75, „ = 5·95

These figures are quite as divergent as those deduced from my observations of the line A; and it will be noticed that the toluene is again intermediate between the simple benzene and the more complicated mesitylene.

But there is another possibility. The specific refraction $\frac{\mu - 1}{d}$ is not absolutely a constant at all temperatures, and it might be supposed that if we were to examine benzene, toluene, and xylene at the same distance from their boiling points, we should find them in perfect harmony. The variation in the case of benzene has been determined with great care. Reckoning the value of carbon in it at the same distances below its boiling point as in the case of the other two hydrocarbons, would indeed diminish the difference, but only by about one-sixth of the whole.

It will be seen by Table III that there are many bodies which show a refraction-equivalent for the line A which is far in excess of that calculated on the supposition that all the double-linked atoms of carbon have the value 6·1. This group comprises the whole of the bodies in which the carbon-atoms actually outnumber the atoms of hydrogen or what may take the place of hydrogen, and includes quinoline, furfuraldehyde, and coumarin.

It may be that these extra carbon-atoms, which of course accord-to our current ideas are combined only with other carbon-atoms, have a value much higher than 6·1; and in the paper already referred to I calculated it for naphthalene, naphthol, phenanthrene, and pyrene, and ventured to assign the provisional value of 8·8. It may be, however, that the excess of the actual over the calculated value is due to the influence of dispersion, for all these substances are enormously dispersive. This is the view of Kanonnikoff, who gives the refraction of naphthalene and several of its derivatives, together with cinnamic alcohol, phorone, and others of this class; but his own figures, calculated on Cauchy's formula, do not bear it out, for the value of C″ for the limit varies in the above-mentioned bodies from 6·54 to 6·2, instead of 5·86.

Yet it is clear that a larger allowance for dispersion should be made than Cauchy's formula will give. The table below contains the refraction-equivalents of the seven hydrocarbons in which the carbon-atoms outnumber the hydrogen-atoms, the proportion of carbon increasing in descending order. The refraction-equivalents are given for the line A, and for an assumed point anterior to A and twice as far from it as D is in the other direction. This is beyond Cauchy's

limit, but fairly within what Langley's observations allow. The two succeeding columns give the value for each carbon, calculated from the two series of refraction-equivalents on the supposition that all the carbons are double linked. For the sake of comparison the values for carbon in benzene, similarly treated, are added :—

Substance.	Formula.	Refraction-equivalent.		Value of each carbon.	
		Line A.	Reduced.	Line A.	Reduced.
Stilbene	$C_{14}H_{12}$	113·39	105·17	6·98	6·41
Diphenyl.....	$C_{12}H_{10}$	89·68	84·96	6·39	6·01
Naphthalene	$C_{10}H_8$	75·14	70·80	6·47	6·05
Diparafluorene	$C_{13}H_{10}$	97·49	91·95	6·50	6·09
Phenanthrene.....	$C_{14}H_{10}$	108·31	101·57	6·81	6·34
Difluorene	$C_{26}H_{18}$	199·87	186·27	6·79	6·27
Pyrene.....	$C_{16}H_{10}$	126·10	114·60	7·07	6·36
Benzene	C_6H_6	43·64	41·88	5·97	5·70

From these figures it would appear not impossible that could we obtain a coefficient of refraction distinct from the coefficient of dispersion, the equivalent of carbon might prove to be the same in these compounds as in the aromatic series, or wherever it is doubly linked. Whether this be the case or not, it is scarcely open to doubt that the enormous increase of dispersion is due to the peculiar manner in which these carbon-atoms are arranged in the compound. I do not believe, however, that we shall be in a position to draw very positive conclusions on this matter till more observations of perfectly trustworthy specimens have been accumulated, and till the phenomena of dispersion have been subjected to a further mathematical investigation.*

The Halogens.

The figures in the table are generally consistent with the values which were originally assigned by me to chlorine, bromine, and iodine, viz., 9·9, 15·3, and 24·5, respectively. These numbers are very nearly the same as those arrived at independently by Haagen, viz., 9·8, 15·3, and 24·8.

* This part of the paper was written before I had seen the two papers of Nasini (*Atti R. A. dei Lincei*, May 1883, March 1884) on the relations between the specific refraction and chemical constitution of organic bodies, containing strictures on the conclusions of Kanonnikoff and his predecessors. With reference to myself, it is evident that Nasini has misapprehended my view of the highest value of carbon.

Oxygen.

As to the refraction-equivalent of oxygen, Brühl was the first to point out that it has two values in organic compounds:—3·4 for the line C where the oxygen is attached to the carbon-atom by double linking; and 2·8 where it is united to two other atoms. There is no doubt that this element has at least two values, but the precise figures may be open to correction. The observations in the table afford but slight means of testing them, unless it be in the case of the alcohols; these, whether monatomic, diatomic, or triatomic, rather favour my old estimate of 2·9 for the line A.

Nitrogen.

In my paper in the *Proceedings of the Royal Society*, it was pointed out that "nitrogen has two values, 4·1 and 5·1, or thereabouts." The lower value is that which was originally assigned to it, and seems to be generally confirmed by the nitriles in Table III. The higher value is where nitrogen exists in organic bases and amides. The evidence from the table is as follows:—

Methylamine,	CH_5N	= 11·5	+ 5·46
Ethylamine,	C_2H_7N	= 19·1	+ 5·37
Diethylamine,	$C_4H_{11}N$	= 34·3	+ 5·06
Triethylamine,	$C_6H_{15}N$	= 49·5	+ 5·12
Allylamine,	C_3H_7N	= 26·3	+ 4·51
Picoline,	C_6H_7N	= 43·5	+ 5·04
Aniline,	C_6H_7N	= 45·7	+ 6·39
Xylidine,	$C_8H_{11}N$	= 60·9	+ 6·15
Formamide,	CH_3ON	= 12·3	+ 5·07

to which may be added from Kanonnikoff:—

Acetamide, C_2H_5ON (24·97 for line C) = 19·9 + 5·07

This indicates a value for nitrogen of about 5·1 in the majority of instances: aniline and xylidine are higher, as might be expected, from their great dispersion. From my old observations, it appears that ammonia in alcoholic solution has an equivalent of 8·97, which again gives 5·07 for nitrogen; but in aqueous solution it was always somewhat higher, averaging in fact 9·50, from which nitrogen could be reckoned at 5·60. It must also be noted that the methylamine and ethylamine in the above list were dissolved in water.

The table contains many instances of the substitution of NO_2 for H. Dealing in the same manner with those whose composition is pretty well understood, we find:—

Nitroethane,	C_2H_5,NO_2	= 16·5 +	11·14
Ethyl nitrate,	C_2H_5O,NO_2	= 19·3 +	11·77
Nitromannitol,	$C_6H_8O_6,6(NO_2)$	= 57·2 +	6(11·99)
Nitrobenzene,	C_6H_5,NO_2	= 43·1 +	12·11
Dinitrobenzene,	$C_6H_4,2(NO_2)$	= 41·8 +	2(12·14)
Nitraniline α,	C_6H_6N,NO_2	= 49·5 +	14·00
Nitrotoluene,	C_7H_7,NO_2	= 50·7 +	12·52
Trinitrotoluene,	$C_7H_5,3(NO_2)$	= 48·1 +	3(13·38)
Nitrobenzoic acid α,	$C_7H_5O_2,NO_2$	= 54·3 +	12·40
„ „ β,	$C_7H_5O_2,NO_2$	= 54·3 +	12·58

In addition to this evidence, we have old experiments giving for NO_2 in ethyl nitrate 11·7, in amyl nitrate 11·9, in nitroglycerol 12·0; and as deduced from metallic nitrates 11·3, which, however, I now consider to be slightly under-estimated. This all tends to show that the refraction-equivalent for NO_2 is a little below 12 in the saturated compounds, and a little above that figure in the aromatic series, where the great dispersion naturally increases the apparent value. The extremely dispersive nitraniline α is included in the list, though it is considerably above the others; but the β variety is excluded on account of its evident nonconformity.

Kanonnikoff determined the refraction of NO_2 mainly on the strength of observations of picric acid, and making allowance for its high dispersive power, he concluded that it was 12·55 for the line C, and that the nitrogen was pentatomic with each of the oxygens united to it by a double bond. This latter conclusion quite accords with my figures; for, taking nitrogen at 5·1, that figure + 2(3·4) = 11·9.

Sulphur.

The two compounds in the table are not without interest. It will be observed that they are highly dispersive bodies. Allyl sulphide seems at first sight to be inconsistent with Nasini's equivalent for sulphur, where it is united with two univalent groups, viz., 14·1; but when the dispersion is taken into account it is rather confirmatory than otherwise. The ethylthiocarbimide gives a figure which, after every possible allowance for dispersion, still transcends the value assigned by Nasini to sulphur where its two valencies are satisfied by the same atom, viz., 15·6, and also exceeds the 16·0, which I originally assigned to this element from the refraction of thiocyanate of potassium and some other compounds.

In bringing this paper to a close, I would briefly draw attention to two points.

1st. *The Phenomena of Dispersion.*—The fourth column in Table III

is very suggestive. It will be observed that the double linking of carbon-atoms, while it does not much affect the specific refraction, widens the spectrum greatly, to such an extent indeed that where there are three pairs of such carbon-atoms, the specific dispersion is about double that of a saturated compound; where, however, the carbon-atoms are actually in excess, the dispersion becomes far more rapid. This will be evident throughout the table, but the following typical hydrocarbons may illustrate it:—

Hexane,	C_6H_{14},	spec. ref.	0·5626,	spec. disp.	0·0242
Amylene,	C_5H_{10}	„	0·5708,	„	0·0300
Benzene,	C_6H_6	„	0·5595,	„	0·0486
Naphthalene,	$C_{10}H_8$	„	0·5870,	„	0·0782
Difluorene,	$C_{26}H_{18}$	„	0·6057,	„	0·1108

or the following alcohols:—

Isobutyl alcohol,	$C_4H_{10}O$,	spec. ref.	0·4878,	spec. disp.	0·0209
Allyl alcohol,	C_3H_6O	„	0·4734,	„	0·0275
Phenol,	C_6H_6O	„	0·5090,	„	0·0476
Naphthol,	$C_{10}H_8O$	„	0·5487,	„	0·0832

The effect of the halogens in lowering both the specific refraction and dispersion is very marked; and that of NO_2 is still more remarkable.

2nd. *The bearing of the optical phenomena on our views of the structure of the compounds.* These optical properties seem capable of deciding with certainty whether an organic body is a saturated compound or not: they indicate also the number of carbon-atoms in that condition which is generally denoted as "double linked;" and they give us a clue as to the mode in which oxygen and nitrogen are combined. The phenomena presented by such bodies as stilbene, cinnamene acetate, and quinoline, lead us to think also that there are influences of structure on the rays of light not yet understood. The last two columns in Table III will suggest many such questions, which I would commend to the consideration of those chemists who more particularly devote themselves to this branch of inquiry.

XXXVIII.—*On the Estimation of Silicon in Iron and Steel.*

By Thomas Turner, Assoc. R.S.M. (Demonstrator of Chemistry, Mason College).

In connection with an inquiry relating to the influence of silicon in iron and steel, it became of the utmost importance to have some method or methods for the rapid and accurate estimation of silicon in various descriptions of iron and steel. All who have had to do with the analysis of iron are aware that the method of estimation by treatment with hydrochloric acid, with or without subsequent evaporation, though commonly adopted, is quite untrustworthy when the percentage of silicon becomes considerable; and the discrepancies observed in different analyses of highly silicious pig-iron, forcibly illustrate the difficulties of the determination. As my experiments also require the preparation of various alloys of silicon and iron, made by melting together mild steel and silicon iron in small crucibles, it is necessary to be able to distinguish between that part of the total silicon found, which existed probably in combination with the iron, and that which exists in the metal in the oxidised condition in the form of slag.

In connection with a work of this kind, one is forcibly struck with the number of methods which have been proposed at various times by different chemists, and also by the fact that few comparisons of the results obtainable by the different processes have been made. In the endeavour to supply this want of comparison, I have taken different specimens of iron and steel, containing various amounts of silicon up to 9 per cent., and have estimated the amount of silicon, not only by the methods most commonly recommended in text-books, but also by certain processes which seemed to give special promise.

Estimation of Total Silicon.

I. A quantity of finely divided metal was treated with strong hydrochloric acid until all action ceased; the solution was evaporated to complete dryness on a water-bath; the residue extracted with hydrochloric acid; the solution filtered off; and the residue well washed, dried, ignited to burn off the carbon, and weighed. This treatment gave tolerably rapid and accurate results with steel, or with iron containing not more than 2·5 per cent. silicon, the effect of manganese in altering the results not being appreciable.

With ordinary pig-iron, the method has the disadvantage of yield-

ing a very bulky residue from which the graphite is not readily burned, and when the percentage of silicon is considerable, it is quite impossible to obtain a pure residue even after boiling with strong hydrochloric acid for many days.

II. The metal was treated with hot strong hydrochloric acid and heated; when all action had ceased, the solution was filtered *without* evaporation, the residue being washed, dried, and ignited as before. Though this method is recommended in certain text-books, probably on account of its rapidity, it has all the disadvantages mentioned in the previous case, and the additional one of leaving part of the silicon in the solution. This fact was mentioned by Drown and Shimer (*Chem. News*, **42**, 299), in a paper on the analysis of iron and steel, in which they prove that "the relative amounts of silicon in solution and in the residue depend on the strength of the acid," less silica being dissolved by a strong than by a weaker acid.

III. The metal was boiled with hydrochloric acid, evaporated to dryness, exhausted with hydrochloric acid, filtered, the residue washed, dried, fused with alkaline fusion mixture, and the silica determined by evaporation to dryness with hydrochloric acid. This method is rather troublesome, but is trustworthy and generally applicable.

IV. The finely divided metal was treated with *aqua regia* and heated if necessary. The solution was evaporated to dryness on a water-bath, the residue extracted, dried, ignited, and weighed. In this case, evaporation takes a longer time, but the graphite burns off more readily. The residue obtained is generally coloured from the presence of a little iron, but the results are fairly accurate with moderate percentages of silicon though somewhat high with larger amounts.

V. In the following process, which was originally recommended by Drown (*Chem. News*, **42**, 331), the metal, which need not be finely divided, is placed in a porcelain dish covered with a watch-glass having a small hole at the edge through which a pipette may be introduced. 25 c.c. of nitric acid, sp. gr. 1·2, are cautiously added, and, when the action has ceased, 5 c.c. of strong sulphuric acid are run in. The solution is evaporated until it solidifies, when water is added and the liquid filtered hot. The residue is washed with strong hydrochloric acid and water, then dried, ignited, and weighed. The silica is snow-white and granular. The results are generally a very little low, and the method has the advantages of rapidity and neatness. It is, however, not applicable with large percentages of silicon and manganese, both on account of the time taken in dissolving, and of the impurity of the residue.

Separation of Slag.

The Chlorine Combustion Process.—This was originally suggested by Wöhler for the estimation of carbon in iron or steel, the metal being heated in a current of chlorine, whereby the iron is volatilised and the carbon left in a state fit for direct combustion in oxygen. Drown and Shimer, in their paper already cited, proposed the application of the process to the separation of silicon from titanium in iron, besides also estimating the carbon as above. Watts (*Chem. News*, **45**, 279; *Chem. Soc. J.*, Abstr., **42**, 1134) subsequently essayed the estimation of carbon, and also the separation of silicon from the mechanically intermingled slag by a modification of the same method.

As proposed by Watts, the method of procedure was as follows:—By a suitable arrangement which he describes, a stream of chlorine is obtained, capable of being easily regulated at the will of the operator; the gas is then carefully dried by means of sulphuric acid, and is freed from air by passing it through a tube filled with lamp-black heated to redness. The iron, which may consist of borings or turnings, is weighed into a porcelain boat, and is introduced into a combustion tube, one end of which is bent at an angle of 110°, and dips into water contained in a flask. When the whole of the air has been expelled and the tube is filled with dry chlorine, it is heated to low redness in a furnace and the stream of gas maintained. The iron is volatilised as chloride and condenses in the cool part of the tube, while the silicon tetrachloride produced at the same time, being volatile, passes into the water and is decomposed. The water on evaporation yields silica, whilst the slag, mixed with carbon, remains unaltered in the boat. This method is stated to "enable the analyst to distinguish absolutely between the elemental and the oxidised portion of the silicon."

The above process appeared to possess such advantages that it was determined to adopt it, the only modifications at first introduced being the use of Ramsay's combustion-furnace, which worked very well, and allowed the whole apparatus to be placed within a moderate-sized fume chamber, and so prevented the nuisance which might otherwise have been produced. All joints and stoppers were coated with paraffin and the leakage rendered quite trifling.

On working the process in this form, however, it was found to be attended with two very great disadvantages. In the first place, as shown by a subsequent table, there was a very considerable deficiency in the total amount of silicon found as compared with the results obtained by the processes mentioned in the early part of this paper; and secondly, the residue left in the boat, even after boiling with dilute hydrochloric acid before burning off the carbon, was found to

contain variable and sometimes considerable amounts of substances other than slag.

The first and most obvious source of loss which presented itself was caused by the adherence of a perceptible quantity of silica to the extremity of the tube used for dipping into the water employed to decompose the silicon chloride, and it was found quite impossible to detach this completely, even by rubbing with a glass rod or the finger. To obviate this, a movable weighed tube was employed to dip into the water, and a considerable improvement was at once observed in the results. This is illustrated in the table given. It will be noticed, however, that the results were still slightly low, and this arose from the obstinate adhesion of a small quantity of silica to the sides of the flask employed, just above the level of the liquid. This was finally overcome by placing the water used for absorption of the silica in a weighed Varrentrapp's bulb. The following table shows the results obtained by the different modifications of the process:—

	Lileshall cold blast pig.	Silicon pig.
Original method	1·17 per cent. SiO_2.	15·31 per cent. SiO_2.
	1·11 " "	15·33 " "
	1·34 " "	15·75 " "
	1·11 " "	—
With movable weighed tube {	2·04 " "	18·32 " "
	2·08 " "	18·83 " "
	2·28 " "	
	2·28 " "	
With weighed Varrentrapp bulb ..... {	2·46 " "	18·86 " "
	2·48 " "	19·17 " "

The above numbers show the actual SiO_2 obtained, including that of the slag, calculated as percentage of iron taken. The amount of silicon is thus multiplied by $\frac{1.5}{7}$, and differences can be more easily noticed. It will be shown subsequently, in another table, that the latter numbers agree very fairly with the total silica obtained by other methods. The manner of procedure was then as follows.

The iron or steel, in large or small fragments, is placed in a porcelain boat and is burned in a stream of dry chlorine free from air. The excess of gas passing through the combustion-tube is washed by passing through water contained in a weighed Varrentrapp's bulb. When the combustion is completed, as indicated by the entire absence of red vapours near the boat, the current is maintained for 5 to 10 minutes, and the solution afterwards evaporated to dryness. The residue is extracted with hydrochloric acid to remove any iron, &c., sometimes carried over, then filtered, washed, and ignited.

The bulb is also weighed, after being carefully dried at 100°. These two weighings together furnish the whole of the unoxidised silicon originally present in the iron. The residue left behind in the boat contains carbon and slag, and also part of the manganese, a little iron as chloride, &c. It may be most conveniently transferred to a test-tube, boiled with a little dilute hydrochloric acid, filtered, dried, and ignited.

This residue often undoubtedly contains slag, since the small rounded pieces may be picked out and examined under the low power of a microscope, and qualitative analysis of the residue yields silica, iron, and calcium. It is, however, still contaminated to a variable extent with other substances, and in every case in which manganese was present in quantity in the original iron, it could also be detected in this residue, which was at first believed to consist wholly of slag. Determinations of the amount of silica present in the residue from different analyses gave very variable results; for while in some cases it agreed very closely in composition with blast furnace slag, in others it showed very considerable differences. Thus blast furnace slag contains pretty uniformly about one-third of its weight of silica, and, while in some cases the silica in the residue varied between 30 and 39 per cent., yet in other cases only 18 per cent. was found, and, in one case, only 5 per cent. of silica was obtained. Further, the mean of ten determinations of slag, by the chlorine process, in Lileshall cold blast grey pig, gave 0·67 per cent., the numbers varying from 0·54 to 0·90 per cent., while two determinations in the same sample by Eggertz' bromine method gave only 0·27 and 0·32 per cent. of slag respectively. Hence it is necessary to estimate the silica present in the residue, by fusion in the ordinary way, before any trustworthy opinion can be formed as to the amount of slag present. When this is done, the results obtained by adding together the total silica found agree with those got by any other trustworthy method.

It may appear to all who have not actually worked the process, that in the form above recommended it must be troublesome and complicated, and there is doubtless some force in such an objection; but it must also be remembered that all methods of separating and estimating the slag are necessarily tedious. The process has been worked side by side with Eggertz' bromine method, and certainly has the advantage both in time and labour. The chief trouble is incurred in first setting up the apparatus, and in the occasional supply of fresh acid, drying tubes, manganese dioxide, &c. But when the apparatus is once in order, a single analysis can be made in three hours, and, if many were required, the time might doubtless be shortened, and a number of analyses may be made with advantage without any attention being required by the apparatus.

The operations are simple and readily performed, while, if Ramsay's burners are employed, and the combustion conducted in a fume-chamber as recommended, no inconvenience is caused in the laboratory, and, as compared with other methods, a considerable saving of time is effected.

The chlorine process appears also to lend itself especially to the rapid and correct determination of silicon in highly silicious pig-iron and in silicon ferromanganese. These varieties of metal burn quite readily in chlorine, and the amount of silicon being high, the experimental error, consequent upon numerous weighings, is much lessened.

In the table which follows is given the percentage of residue, consisting chiefly of silica obtained by the various processes before mentioned. Of the numbers referring to the chlorine process, the first line gives the total silica, while the last line gives the percentage of slag.

	Siemens-Martin mild steel.	Lileshall cold blast grey pig.	Denby hot blast grey pig.	S. Staffordshire No. 1 grey pig.	Welsh silicon ferro-manganese.	Silicon, pig.
I. With HCl, and evaporation	0·04	2·53 2·51	6·72	14·23	22·00	20·24
II. With HCl, without evaporation		2·37 2·37				
III. With HCl, evaporation and fusion		2·58		11·56		
IV. With HCl + HNO_3, and evaporation	0·03	2·45	6·21	11·40	21·56	19·23
V. Drown's method, ($HNO_3 + H_2SO_4$)	0·04	2·40 2·43	6·03 6·07	11·42	23·32	18·79
Chlorine process, with Varrentrapp bulb	0·06 0·00	2·46 0·66	6·16 0·25	11·45 0·33	21·41 0·49	19·17 0·76

It will be noticed that the amount of slag increases as the percentage of silicon becomes greater. The larger quantity present in the cold-blast pig may possibly be due to the lower temperature of the iron in the furnace during the separation of the slag.

In conclusion, from the above results and from the experiments mentioned earlier in the paper, I infer—

1. That methods I, III, IV, and V give fairly concordant results with steel and ordinary cast iron, while of these four the method proposed by Drown has the advantages of most rapid action, least bulky residue, and most easily burned graphite.

2. That for silicon pig and silicon ferromanganese, methods I, II,

and V are quite inapplicable, while III and IV give moderately accurate results; but all these methods are incapable of distinguishing between oxidised and unoxidised silicon.

3. That the chlorine process, in the modified form above suggested, has the great advantage of distinguishing between the unoxidised silicon and slag, whilst it is rapid and fairly accurate with all classes of iron, and hence may help to supply a long-felt want of the iron and steel analyst.

XXXIX.—*Note on the Melting Points, and their Relation to the Solubility of Hydrated Salts.*

By William A. Tilden, D.Sc., F.R.S.

In a paper read before the Royal Society last June, and since printed in the *Philosophical Transactions*, Mr. Shenstone and I drew attention to the relation observable in the solubility of salts in water at temperatures above 100°, and the melting points of the same salts in the anhydrous state. This relation may be exhibited by representing the solubilities graphically in the usual manner, when it is noticed that the curves of solubility of the most fusible turn up most rapidly, whilst the solubility of those less fusible increases nearly in proportion to the temperature, and the curves therefore approach a straight line. This is well seen in the case of two such salts as potassium chloride and potassium chlorate, or sodium chloride and potassium nitrate.

Feeling satisfied that the connection between fusibility and solubility observed in the salts referred to would be found to exist in other cases, I have lately been inquiring into the points of fusion of hydrated salts and their solubility below these temperatures. Very few of the melting points of salts containing water of crystallisation could be found recorded, and I have therefore had to make a number of experiments. For assistance in this, and in the determination of solubility in a few cases, I am indebted to Mr. George Lloyd, lately a student in the Mason College Laboratory.

The melting points were ascertained in the following manner:—Near to one end of a piece of tubing, drawn out very thin, and about a millimeter in diameter, a narrow strip of moist filter-paper was introduced, and the end then sealed. The tube was then bent twice at right angles, and into the upright open end was dropped a small

clear crystal or fragment of a crystal of the salt, and the tube was then attached to a thermometer. Some preliminary trials having indicated the melting point of the salt within a few degrees, the thermometer and tube were stirred round in water or sulphuric acid a little below that temperature, and contained in a beaker placed over a lamp. The object of the damp paper at the bottom of the tube is to supply water-vapour, and so diminish the tendency of the salt to effloresce.

In many cases the melting point can be thus determined within half a degree, but though several experiments were made in each case, the observations make no pretence to great accuracy. This is due chiefly to the fact that many salts are resolved into a mixture of liquid and solid, and the temperature at which this occurs is sometimes difficult to observe. The fact is these salts seem to be incapable of entering into true fusion, the partial liquefaction being the result of the formation of a crystalline hydrate containing a smaller proportion of water. This happens notably with the sulphates of zinc, cobalt, nickel, and iron. On the other hand there is often no sign of dissociation, as in the alums and many other salts, if the experiment is carefully performed. Of the following salts, the melting points have been given in two or three cases by other observers, but, except where an authority is mentioned, I have verified them all.

Simple Sulphates—	m. p.
$MgSO_4,7H_2O$	70°
$ZnSO_4,7H_2O$	50°
$CoSO_4,7H_2O$	96—98°
$NiSO_4,7H_2O$	98—100°
$FeSO_4,7H_2O$	64°
$MnSO_4,5H_2O$	54°
$CdSO_4,\frac{8}{3}H_2O$	D*
$CuSO_4,5H_2O$	D
$Al_2(SO_4)_3,18H_2O$	D
$Na_2SO_4,10H_2O$	34°
Double Sulphates—	
$KAl(SO_4)_2,12H_2O$	84·5°
$NH_4Al(SO_4)_2,12H_2O$	92°
$NaAl(SO_4)_2,12H_2O$	61°
$RbAl(SO_4)_2,12HO$	99°
$CsAl(SO_4)_2,12H_2O$	105—106°
$KCr(SO_4)_2,12H_2O$	89°†
$Co(NH_4)_2(SO_4)_2,6H_2O$	D

* D = gives off its water without melting.

† Converted into green salt.

	m.p.	
Double Sulphates—		
$Ni(NH_4)_2(SO_4)_2,6HO_2$	D	
$NiK_2(SO_4)_2,6H_2O$	D	
$MgK_2(SO_4)_2,6H_2O$	D	
$Mg(NH_4)_2(SO_4)_2,6H_2O$	D	
Chromate—		
$Na_2CrO_4,10H_2O$	23°	(Berthelot).
Arsenate—		
$Na_2HAsO_4,12H_2O$	28°	
Phosphate—		
$Na_2HPO_4,12H_2O$	35°	
KH_2PO_4 (anhydrous)	96°	
Chlorides—		
$BaCl_2,2H_2O$	D	
$SrCl_2,6H_2O$	112°	
$CaCl_2,6H_2O$	28°	
Carbonate—		
$Na_2CO_3,10H_2O$	34°	
Oxalates—		
$H_2C_2O_4,2H_2O$	98·5°	
$(NH_4)_2C_2O_4,H_2O$	D	
Acetates—		
$NaC_2H_3O_2,H_2O$	58·5°	
$Cu(C_2H_3O_2)_2,H_2O$	D	
Borate—		
$Na_2H_2B_4O_8,9H_2O$	75·5°	
Theiosulphate—		
$Na_2S_2O_3,5H_2O$	48·5°	
Nitrates—		
$Ca(NO_3)_2,4H_2O$	44°	(Ordway)
$Mg(NO_3)_2,6H_2O$	90°	„
$Ni(NO_3)_2,6H_2O$	56·7°	„
$Cd(NO_3)_2,4H_2O$	59·5°	„
$Zn(NO_3)_2,6H_2O$	36·4°	„
$Mn(NO_3)_2,6H_2O$	25·8°	„
$Ca(NO_3)_2,6H_2O$	26·4°	„
$Cu(NO_3)_2,3H_2O$	114·5°	„

The temperatures given above, at which incipient fusion occurs, are in many cases the temperatures at which the turning point in the

curve of solubility occurs. It appears therefore probable that the crystallised hydrates, even when in solution, are completely dissociated within comparatively narrow limits of temperature. One of the most striking examples is of course sodium sulphate, but similar phenomena are exhibited by sodium carbonate and chromate, and by manganous, ferrous, and other sulphates. This dissociation must also be the cause of the fact that the solubility at or about the melting point of so many salts is less than would be otherwise expected. It must, however, be pointed out that salts like sodium sulphate and phosphate, which may be melted in their water of crystallisation, are miscible with water at the same temperature in all proportions, in other words the solubility of the crystallised salt is infinite. Hence there must be something wrong in some of the recorded solubilities of such salts at these temperatures.

If we take from the list salts which are isomorphous with one another and contain the same amount of water of crystallisation, and which alone are comparable amongst themselves, we find that the solubility and fusibility stand in the same order at all temperatures below the point of fusion or dissociation of the hydrate.

The following are examples:—

The solubility is taken to be the weight of crystallised salt dissolved in 100 parts of water:—

Zinc and Magnesium Sulphates.

		Solubility at		
	m.p.	0°.	40°.	50°.
Zinc.....	50°	115·2	224	263·8
Magnesium....	70°	72·4	178	212·6 (at 49°)

Alums.

		Solubility at			
	m.p.	0°.	17°.	20°.	50°.
Sodium	61°	110	—	—	—
Potassium	84·5°	3·9	—	15·13	44·11
Rubidium.....	99°	—	2·27	(Redtenbacher, *Watts's*	
Cæsium	105—106°	—	0·619	*Dict.*, **5**, 580—583).	

Sodium Arseniate and Phosphate.

		Solubility at	
	m.p.	0°.	20°.
Arsenate	28°	17·2	140·7 (at 21°)
Phosphate	35°	6·5	27·2

Calcium and Strontium Chlorides.

	m.p.	Solubility at 0°.	Solubility at 40°.
Calcium	28°	165·7	7141·0
Strontium	112°	106·2	205·8

Information is yet wanting as to the solubility of many of the salts in the list.

It is of course not maintained that fusibility is the sole cause of solubility, for amongst the commonest phenomena of solution are very many difficulties which cannot be explained away. But there can be no doubt that fusibility and solubility are closely connected together, and I have ventured to bring the subject under the notice of the Society, because it can scarcely be advanced any further till a much greater store of experimental data has been accumulated.

XL.—*On Calcium Hydrosulphides.*

By Edward Divers, M.D., Principal, and Tetsukichi Shimidzu, M.E., Research Assistant, Imperial Japanese College of Engineering, Tokio.

Calcium Hydrosulphide.

We have succeeded, after many trials, in establishing the existence of normal calcium hydrosulphide by getting it in the solid state. Although often referred to in connection with the recovery of sulphur from alkali-waste, and with the purification of coal-gas by lime, this substance has remained unknown till now except in dilute solution.

Pelouze (*Compt. rend.*, **62**, 108; *Handw. Ch.*, **2**, 353) endeavoured to prepare it by treating calcium hydroxide in the form of milk of lime with a current of hydrogen sulphide gas, and concluded that a solution could only be obtained in this way which held no more than 7 per cent. of it. He also found that he could prepare more concentrated solutions by using calcium sulphide or a solution of sugar-lime. We find, on the other hand, that calcium sulphide acts much more slowly than lime in yielding concentrated solutions of the hydrosulphide.

Böttger's directions (*Annalen*, **29**) for preparing calcium hydrosulphide for use as a depilatory, which are copied into many works

on chemistry and pharmacy, are misleading, as, according to them, hydrogen sulphide is to be passed into thin milk of lime until the mass acquires a bluish-grey colour. The production of this colour is due to the formation of ferrous sulphide, and this must take place as soon as any soluble sulphide is present, and before, therefore, any quantity of lime has been acted upon by the hydrogen sulphide. As to the mass thus obtained, which is to be smeared upon hides as a depilatory, the little true hydrosulphide in it is in solution in the liquid part of it. Only last year a similar misapprehension appeared in a paper by Lewis T. Wright (*J. Soc. Chem. Ind.*, **2**, 122), in which he states that he prepares calcium hydrosulphide by saturating moist calcium hydroxide with hydrogen sulphide, and then uses the product in the place of soda-lime in the determination of nitrogen in nitrates. The product he uses cannot contain any solid calcium hydrosulphide. Gas-lime, too, is not calcium hydrosulphide, as commonly described.

Calcium sulphide has long been known to yield some calcium hydrosulphide in solution when heated with water, and to yield it in the drainings from soda-waste heaps. From the interior of a heap of waste, which had been lying for months, Kraushaar (*Chem. Soc. J.*, **34**, 171; *Dingl. polyt. J.*, **226**, 412) dissolved out by cold water more than 3 per cent. of the sulphur, and found nine-tenths of this to be in the form of hydrosulphide. This, however, must have been partly in the form of sodium salt. By heat under pressure, according to Kraushaar (*loc. cit.*), confirmed by Curphey, most of the sulphur of soda-waste can thus be dissolved out; but according to Schaffner (*Lunge's Alkali Manuf.*, **2**, 658—659), Chance (*J. Soc. Chem. Ind.*, **2**, 11), and Weldon (*ibid.*), the solution is only partial unless very much water is employed.

Preparation of Calcium Hydrosulphide.

Nothing can be simpler in the abstract than the preparation of calcium hydrosulphide, consisting, as it does, in treating calcium hydroxide with hydrogen sulphide in presence of a sufficiently small quantity of cold water, and then crystallising the solution. But the details of the process require much attention, and this fact probably explains how it is that the hydrosulphide has not hitherto been obtained. The difficulties of its preparation depend upon its instability and exceeding solubility in water.

If hydrogen sulphide is forced through a semi-solid mass of calcium hydroxide and water, the whole will become liquefied and increased in volume. To this clear solution much lime has still to be added, and dissolved by hydrogen sulphide, before a saturated solu-

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tion is obtained. This lime might be added as hydroxide, but it is practically requisite to use the oxide, as, unless the hydroxide were dry, too much water would be yielded by it, and if it were not in fine powder troublesome lumps would form from it, and the operations of drying and pulverising thus required would probably be attended with carbonatisation by the atmosphere. Quicklime prepared from precipitated calcium carbonate is almost necessary for preparing the hydrosulphide. That made from calcite may, after grinding, be used for making a moderately concentrated solution, but it is too difficult of dissolution by hydrogen sulphide to be convenient for making a saturated solution.

The preparation of a crystallising solution of calcium hydrosulphide takes days to complete, and all through the process air must of course be excluded. In hot weather it is hardly possible to prepare it without cooling down, and at all seasons cooling with snow or ice facilitates the process.

The lime we used was made by igniting, in platinum crucibles, calcium carbonate which had been precipitated from an alkaline alcoholic solution of fused calcium chloride. It was always found free from sulphate and carbonate, but was never so pure as to dissolve in the large proportions required without leaving some small residue. We believe, indeed, that dissolution to saturation by hydrogen sulphide will be found a more delicate wet test of the purity of lime than any other.

We tried hydrogen sulphide prepared from several sources, but ended by using the ordinary gas from iron sulphide, washed, and filtered through a column of cotton, and sometimes dried with calcium chloride.

The vessels we finally employed for making crystallising solutions were formed out of tubing 18—20 mm. in diameter. The body of the tube was about $1\frac{1}{2}$ decimetres in length, and ended in long drawn-out limbs of about 5 mm. in diameter. One of these was bent acutely just beyond its origin in the main part of the tube. The tube being fixed in a nearly vertical position, with its bent limb below, the gas could be sent through this limb up from the very bottom of the liquid, and thus made to keep the undissolved lime well agitated. Occasionally when working with almost finished solutions, a stout platinum wire was, without stopping the current of gas, pushed down the upper straight limb of the tube into the solution to detach adhering matters. Except at these moments, and when adding more lime, the exit-tube was always in connection with a wash-bottle, serving as a guard against the entrance of air.

Before setting the solution to crystallise, it had to be left to clarify by the subsidence of excess of lime and of the impurities always

present in small quantities. It had then to be decanted into a crystallising tube. This was done in a stream of hydrogen sulphide, after the tube had been turned to the horizontal position to avoid bubbling of the gas and disturbance of the sediment. The two tubes were connected by black rubber tubing during the decantation. The mouths of the crystallising tube were afterwards closed by caoutchouc caps coated with paraffin, but, except for the few moments occupied in transferring, the solution touched glass only.

In order to prepare a solution of the necessary concentration, between two and three parts only of water must be used with one of calcium oxide. But as large a proportion as that may be added, and yet through evaporation from the hot mass, nearly dry calcium hydroxide be obtained. Evidently, therefore, the addition of this amount of lime to the water must be made gradually. To start with, 1 part of lime dropped into somewhat less than 4 parts of hot water gives, from the purity and fine division of the lime, about the stiffest paste of hydroxide that can be worked with. The mixing must be done in the preparation-tube itself. Thin milk of lime may be used instead, but in that case a larger quantity of lime will have to be added afterwards. In the thick paste dissolution of the hydroxide proceeds, with evolution of heat, and with comparative rapidity, along the channels which the hydrogen sulphide works out for itself in forcing its way through the paste. Admixture of the undissolved mass of the hydroxide with the concentrated solution thus formed, is attended with evolution of heat, and the replacement of hydroxide by so abundant a crystalline precipitate of hydrated sulphide as to render the whole very thick again.

Dissolution of the first quantity of lime having become complete, fresh lime is added to the clear thin liquid. The lime reacts more mildly with the solution than with simple water. If very well agitated, the lime passes gradually into a slimy matter, consisting probably of very fine crystals, before it passes into solution. Often, however, some crystalline lumps form, which, however, very slowly, even if left at rest, break down into the slimy matter. When calcite-lime is used, hard crystalline masses generally form, which are afterwards practically irreducible, so that such dense lime is hardly to be used successfully. The lime dissolves best when added gradually, and is then less likely to choke up the tube with hard crystalline sulphide. We have found it necessary to make additions of lime about four times, in order to reach the point of saturation, and leave some excess in proof of having done so. We have already described the decantation of the formed solution from this excess and the small unavoidable impurities.

If the liquid is kept cold during the passage of the gas, in order to

favour reaction, crystals of the hydrosulphide at last form in abundance; but this is not the case at ordinary temperatures. Saturation to the crystallising point being reached, the current of gas is stopped, and the liquid left in the tube to clarify, very carefully sealed up, at the ordinary, or a slightly warm temperature, in order that most of the crystals which may have formed in the cold shall redissolve. After decantation, the clear solution is again kept in ice, when it crystallises, and the more abundantly the better it has been saturated at a low temperature.

The calcium hydrosulphide thus obtained is separated from its mother-liquor by draining and blowing a current of hydrogen sulphide through the mass of crystals, the tube being all the while immersed in snow. They cannot be removed from an atmosphere of hydrogen sulphide without undergoing change, and admit therefore of no further drying, except by a momentary swinging of the tube to expel adhering liquid centrifugally. In warm weather, the crystals evolve hydrogen sulphide even in an atmosphere consisting of that gas.

Properties of Calcium Hydrosulphide.

Calcium hydrosulphide forms colourless prismatic crystals. It melts on a slight rise of temperature, in its water of crystallisation, but not without decomposition beginning, even in an atmosphere of hydrogen sulphide. Most probably, it never itself undergoes oxidation by the air, but decomposes into other compounds before that change can take place.

It is exceedingly soluble in water and in alcohol, so much so indeed, that a fourth of its weight of water at ordinary temperatures appears to be more than sufficient to hold it in solution. The addition of four or five drops of water to 10 c.c. of saturated solution entirely destroys its power of crystallising when cooled in ice. There is, however, nothing singular in this, as all salts with much water of crystallisation show the same behaviour in close vessels at temperatures near that of their aqueous fusion.

An almost saturated solution, even when warm, loses no water, or scarcely any, in a current of dry hydrogen sulphide. Thus, gas previously dried, passed in a steady stream for four hours through a slightly warm solution, gave only $4\frac{1}{3}$ mgrms. increase in weight to a calcium chloride tube, through which it passed on leaving the solution.

The specific gravity of one solution, which proved on analysis to hold 32 per cent. anhydrous, or 64 hydrated, salt, was found to be 1·255 at 23° C., and that of another holding $37\frac{1}{2}$ per cent. anhydrous, or $75\frac{1}{2}$ per cent. hydrated, salt in solution, 1·310 at $23\frac{1}{2}$°. The solu-

tions are colourless, and similar in degree of liquidity to other concentrated saline solutions.

Other properties of calcium hydrosulphide are described in the succeeding sections of this paper.

Composition of Calcium Hydrosulphide.

The existence of calcium hydrosulphide in solution has long been admitted, and is sufficiently established by the qualitative reactions of the solution. The nature of the crystals now described is equally well shown by the same means. Their free solubility in water and alcohol proves the absence of hydroxide. The absence of colour proves the absence of polysulphides. The precipitation of all the sulphur by zinc salts, and the solubility of the crystals in alcohol, already adduced, prove the absence of oxidised sulphur salts. The liberation of hydrogen sulphide by manganous salts proves the presence of basylous hydrogen and the solubility in alcohol, by showing the absence of calcium oxide, hydrated or not, proves that the hydrogen is in equivalent amount to the calcium. All this stands true without seeking support from the analogy to other compounds and reactions. We have not, however, failed to recognise the importance of quantitative determinations, and have made a number of analyses both of solutions and of crystals. Our difficulty has been to prepare samples for analysis.

A mixture of sulphur-free potassium hydroxide and potassium hypobromite was used as the oxidising agent. The solution was weighed by difference, directly into potassium hydroxide solution, the weighings being made in a Sprengel's specific gravity tube. The crystals were weighed in the tube in which they had been made. The oxidation by the hypobromite was immediate and complete in the cold, but as a precaution heat was applied. The calcium was precipitated as oxalate, and the sulphur as barium sulphate.

0·836 gram of a solution of specific gravity 1·255 at 23° gave calcium 11·96 per cent., and sulphur 19·26 per cent. Two atoms of sulphur to one of calcium, taking this as 11·96, would be 19·14.

Of another solution, specific gravity 1·310 at 23½°, 0·594 gram gave calcium 13·76 per cent., and 0·818 gram gave sulphur 22·85 per cent. It was difficult to weigh off these solutions with a high degree of accuracy, so that calcium and sulphur would better have been estimated in the same portion. The results, however, give to 100 atoms of calcium 207 of sulphur, leaving therefore no room to doubt as to the facts.

The attempt to remove mother-liquor from some good crystals by rapidly effected pressure between blotting-paper, gave results which

were sufficiently definite in their indication, but which showed only a little more than 7 atoms of sulphur instead of 8, to 4 of calcium. The analysis was made upon only 0·2566 gram, and yielded quantities corresponding to calcium 20·07 per cent., and sulphur 28·32 per cent.

A quantity of good crystals from another preparation was weighed while still wet with mother-liquor. It amounted to 3·275 grams, and gave calcium 16·47 per cent., and sulphur 26·11 per cent., making 33 atoms calcium to 65 atoms sulphur. To have been 2 atoms to 1 calcium, the sulphur should have been found 26·35 per cent. instead of 26·11 per cent.

Other analyses made, were only for the determination of the water of crystallisation. The crystals, dried on blotting-paper, and partly decomposed in consequence, had given results already stated, which correspond to $6H_2O$. Calculation for a mixture of $99(CaH_2S_2,6H_2O)$ with $13CaH_2O_2$, gives exactly 20·07 per cent. calcium as found, and 28·39 per cent. sulphide instead of 28·32 per cent. as found. The water here shown present may be safely taken as not less than the water of crystallisation; for, by an experiment, also already described, it had been proved that a cold saturated solution does not evaporate in a current of dry gas, and from this it stands still more certain that the water of the crystals will not escape at common temperatures.

By a determination of calcium in another preparation of good crystals, successfully drained while ice-cold, we obtained, using 0·9455 gram, 17·54 per cent., which corresponds with about $6\frac{4}{5}$ molecules of water. The adoption of $7H_2O$ as expressing the water of crystallisation, would need the assumption that the crystals, wet as they were, had lost much hydrogen sulphide, and this cannot be admitted. On the other hand, the adoption of $6H_2O$ makes more than 5 per cent. of water of solution to be present with the crystals, corresponding with perhaps as much as 15 per cent. solution at or near 0°, and this assumption may be admitted as quite probable.

We conclude, therefore, from our experiments, that calcium hydrosulphide crystallises almost certainly with 6 mols. of water, and is therefore formulated by $CaH_2S_2,6H_2O$.

*Calcium Hydroxyhydrosulphide; its Preparation.**

The decomposition of a solution of calcium hydrosulphide was stated by Berzelius to yield calcium sulphide, and by Pelouze to yield hydroxide. Both observations will have been correct, the calcium sulphide

* *Hydrated Calcium Sulphide.*—The remarkable results of Lunge and Naef's investigation of the constitution of the chlorides of lime and of lithia (*Annalen*, **219**, 129) have placed Odling's formula for the lime compound, ClO.CaCl, quite beyond the region of legitimate doubt, as against the formula $CaCl_2,CaO_2Cl_2$, and

being understood to be hydrated. The hydrosulphide becomes the hydroxyhydrosulphide in concentrated solutions, hydroxide in weak ones, and mixtures, or possibly compounds of the two, when the solutions are of medium strength, while the hydroxyhydrosulphide itself becomes hydroxide by the action of water. These decompositions proceed only when the hydrogen sulphide produced can escape or become diluted, and are much more rapid and complete in hot solutions than in cold solutions.

Nothing else, we believe, has been published concerning calcium sulphide formed in the wet way, besides Berzelius' statement of its occurrence in acicular crystals. As we find it to be hydrated, and different in its behaviour with water from true calcium sulphide, we follow all analogy in describing it as calcium hydroxyhydrosulphide, symbolised by Ca(SH)(OH). It is certainly of common, though unrecognised occurrence in the arts.

Calcium hydroxyhydrosulphide is formed from the hydrosulphide by the reaction of this salt with water:—

$$CaS_2H_2 + OH_2 = Ca(SH)(OH) + SH_2,$$

or with calcium hydroxide:—

$$CaS_2H_2 + CaO_2H_2 = 2Ca(SH)(OH).$$

It is also formed by the union of water with calcium sulphide, as in the interior of heaps of soda-waste, and by the reaction between calcium hydroxide and hydrogen sulphide, as in coal-gas purification. The first of these modes of formation may also be properly regarded as a process of dissociation, as the water yielding the hydroxyl is already a part of the crystals of the hydrosulphide.

Even in a closed vessel, when an ice-cold saturated solution of calcium hydrosulphide, having crystals of the salts lying in it, is merely allowed to rise to a summer temperature, it effervesces a little from this decomposition, the crystals at the same time melting. But when exposed to the air, calcium hydrosulphide begins at once to change rapidly into the hydroxyhydrosulphide. Its crystals

there can therefore be, as regards the bivalent nature of calcium, no hesitation in adopting for the hydrated calcium sulphide the constitutional formula HS.Ca.OH.

According to Sabatier (*Compt. rend.*, **89**, 234; *Chem. Soc. J.*, **36**) the admixture of a solution of the hydroxide with one of the hydrosulphide of potassium or sodium is not accompanied by evolution of heat, unless indeed the solutions are very concentrated, and then only to a slight extent. The so-called monosulphides of these metals in the form of hydrated crystals seem therefore to have no sufficient claim to their title, and should rather be regarded as combinations of hydroxide with hydrosulphide under the influence of forces of crystallisation—

KSH,KOH, rather than K_2S,H_2O.

retain their shape for a time, but quickly grow dull and crusted on the surface. Beneath the crust they deliquesce, and thus become a liquid mass enclosed in a pasty shell. Although, as already mentioned, they lose no water by evaporation, they yet decrease in weight very quickly during deliquescence by evolving hydrogen sulphide.*

Decomposition of concentrated solutions of calcium hydrosulphide exposed to the air, is not less remarkable than that of the crystals. The solution becomes almost instantly crusted over with crystals, and if a current of air is passed through it an abundant precipitation of crystals, which as well as those of the crust are calcium hydroxyhydrosulphide, is the result. The simultaneous oxidation which occurs is relatively slight, while absorption of carbon dioxide appears not to take place at all. (See a subsequent section of this paper.) All oxidation may, however, be avoided by exposing the solution to an atmosphere of hydrogen, or to a stream of this gas instead of air.

The reaction of a solution of calcium hydrosulphide with calcium hydroxide has already been referred to in describing the preparation of the hydrosulphide. Where the lime used has been prepared from precipitated carbonate, and it is kept well agitated in the solution, it becomes rapidly converted into a crystalline translucent precipitate, much more bulky than itself. With insufficient agitation, this lime may at first form crystalline lumps, but these are not permanent. When, however, dense calcite-lime is taken, the reaction proceeds very slowly, and if this lime be left lying in the solution, it is gradually replaced by relatively large prismatic crystals of the hydroxyhydrosulphide, some of which shoot up into the liquid above. This mass of crystals is permanent in the mother-liquor.

* This is the second salt made known by one of us that *deliquesces with loss of weight* when exposed to air, and from the same cause, decomposition with liberation of water. The other salt is normal ammonium carbonate, which decomposes into ammonia, acid ammonium carbonate, and water for the most part liquid—$CO_3(NH_4)_2OH_2 = NH_3 + CO_3H.NH_4 + OH_2$ (*Chem. Soc. J.*, **23**, 185).

The resemblance between barium hydrosulphide and calcium hydrosulphide is very close, except perhaps in the property of stability. Both crystallise on cooling their solutions in prisms having water of crystallisation,—how much in the case of the barium salt is unknown. Crystals of the barium salt are stated to effloresce in the air, and their solution, when heated, to lose hydrogen sulphide; probably, therefore, the efflorescence, like that of the calcium salt, is due not to loss of water, but of hydrogen sulphide. Yet solid barium hydrosulphide is said to lose water when heated, and only at an incipient red heat to lose hydrogen sulphide, and become the sulphide. The correctness of this statement may, however, fairly be doubted, when the action of water upon this salt and upon the hydroxyhydrosulphide is considered.

Properties of Calcium Hydroxyhydrosulphide.

Calcium hydroxyhydrosulphide occurs in colourless four-sided prisms, which are sometimes of size, but are generally in exceedingly minute needles, detached or crusted together, or, when they have been formed by a graduated exposure of the solution to the atmosphere, arranged in stellate groups. Deprived quickly of their mother-liquor, the crystals may be obtained dry with scarcely any appearance of change. They gradually, however, become opaque from decomposition, although they retain their silky lustre for a comparatively long time. Calcium hydroxyhydrosulphide slowly evolves hydrogen sulphide in the air, and becomes yellow by absorption of oxygen. It also takes up carbon dioxide from the air, but not very freely at first. It contains water of crystallisation, which it loses when heated, but not without partial decomposition.

It dissolves readily in water, but the solution almost immediately decomposes into hydroxide, which is precipitated, and hydrosulphide, which remains in solution. It is insoluble in a moderately concentrated solution of calcium hydrosulphide, and unaffected by it. It is insoluble in alcohol, and is slowly decomposed by this liquid, as by water, hydrosulphide becoming dissolved out. From the readiness with which calcium hydroxyhydrosulphide is converted into hydroxide, preparations of it are apt to be largely mixed—or possibly combined—with hydroxide.* Such preparations often show very little appearance of having become so much changed in composition.

In describing the preparation of the hydrosulphide, we have already indicated that the hydroxyhydrosulphide reacts with hydrogen sulphide to reproduce the hydrosulphide.

Composition of Calcium Hydroxyhydrosulphide.

The decomposition of the hydroxyhydrosulphide by water into

* A tube containing a nearly saturated solution of calcium hydrosulphide, and having its ends closed by caoutchouc caps coated with paraffin, was left aside during the winter months. The solution had then become, for the most part, converted into transparent colourless crystals of hydroxyhydrosulphide and a non-crystalline pellicle on its surface and on the walls of the tube. The residual solution was only moderately yellow, so that very little oxidation had occurred, while, on opening the tube, air rushed in, showing that the tube had become partly vacuous. The gas remaining in it was hydrogen sulphide. The pellicle was a very singular body. It was insoluble in water, and apparently only slowly affected by washing. It had a porcellanous whiteness and translucency, and was remarkably tough, more like an animal membrane than an inorganic salt. Washed and dried at a moderate heat, it still preserved much of its tenacity, and when moistened, again assumed its membranous character. When ignited in a tube, it lost some water and hydrogen sulphide, but still retained its form. A qualitative examination of it satisfied us that it was a basic hydroxyhydrosulphide.

hydrosulphide and hydroxide, its freedom from colour, mode of formation, transparent solution in hydrochloric acid, and the complete precipitation of its sulphur by manganous salts, prove it to be a compound (or mixture) of hydroxide and hydrosulphide. All that is further necessary, therefore, is the quantitative estimation of the sulphur and the calcium.

Some calcium hydrosulphide solution was exposed for an hour or more to the air, and the crust of crystals which formed during this exposure was lifted off with a spatula, washed quickly with only a little water, and analysed without drying. An unweighed quantity gave 0·0644 gram calcium and 0·0515 gram sulphur, quantities which are in the atomic proportions of these elements.

Two other preparations were separately made, and as the mother-liquor of the hydroxyhydrosulphide is only a solution of hydrosulphide, any portion of which adhering to the crystals must become hydroxyhydrosulphide also, while washing with water decomposes the crystals, these preparations were simply drained on porous tiles without any washing, and with great success, judging from their appearance. The analyses, made upon 1·5993 grams and 0·6630 gram, gave—

	I.	II.	$CaSH.OH,3H_2O$.
Calcium	27·48	27·85	27·78
Sulphur	21·49*	22·05	22·22
Water	—	—	50·00
			100·00

An analysis was made of the cleanest crystals we could prepare by the reaction between solid calcium hydroxide (or oxide?) and solution of the hydrosulphide; but, in accordance with what we have stated concerning this method of preparing the hydroxyhydrosulphide, we had to use the dense calcite-lime in order to get a growth of crystals, and the crystals thus obtained proved to be impure, two-sevenths of the calcium being, not hydroxyhydrosulphide, but, for the most part, still hydroxide.

It will be seen from our analyses of the hydrosulphide and the hydroxyhydrosulphide, that the two salts may be written thus:—

Hydrosulphide. $Ca^{SH,3OH_2}_{SH,3OH_2}$

Hydroxyhydrosulphide.† $Ca^{SH,3OH_2}_{OH}$

* A slight loss of barium sulphate occurred in this case.

† Barium hydroxyhydrosulphide is well known, but under the designation of hydrated barium sulphide, just as the hydroxide was once styled the hydrated oxide. Like the calcium salt, barium hydroxyhydrosulphide occurs in minute crystals having water of crystallisation, and dissolving in water, with subsequent

Calcium Monosulphide.

True calcium monosulphide, as distinguished from the hydroxy-hydrosulphide, can be obtained, but mixed with some hydroxide, by gently heating the hydrosulphide in a current of hydrogen sulphide. Thus produced it is a white amorphous solid. It dissolves without much difficulty in water, differing therein from the sulphide of the furnace, in consequence, no doubt, of less density, and fine state of division. In dissolving, it must be assumed to pass into the hydroxy-hydrosulphide. The first stage of the decomposition of the hydrosulphide by heat, as already pointed out, is into hydroxyhydrosulphide. This, then, if enough water is present, changes into hydroxide, but in the absence of water into sulphide—

$$\text{1st.}\quad CaS_2H_2 + H_2O = CaSH.OH + H_2S$$

$$\text{2nd.}\quad \begin{cases} CaSH.OH + H_2O = CaO_2H_2 + H_2S, \text{ or} \\ CaSH.OH = CaS + OH_2. \end{cases}$$

Both forms of the second stage occur in the decomposition of the crystals of hydrosulphide, as shown by the experiment we now describe, in which about one-fifth of the calcium became hydroxide, and the rest sulphide.

Having prepared some crystals of hydrosulphide in a tube, the tube with its contents was weighed, and, by deducting the weight of the empty tube afterwards, the weight of the salt was ascertained to be 0·9455 gram. A stream of well-dried hydrogen sulphide was then passed through the tube and maintained to the end of the experiment. The tube was heated for a time at 65°, and then to 100°, at which it was kept for three hours. The residue was amorphous and very white, except at the edges, where it was yellow from oxidation. This oxidation had occurred for the most part during the preparation of the crystals. The calcium and sulphur in it were both determined. It agreed closely in composition with a mixture expressed by the formula $5CaS + \frac{1}{10}CaS_4 + CaO_2H_2$, the polysulphide being due to accidental atmospheric oxidation—

conversion into hydroxide and hydrosulphide. This shows how improbable it is that the hydrosulphide can without any decomposition lose its water of crystallisation by heat. Its composition is expressed by the formula $BaOH(SH),5H_2O$. Like the calcium compound, it forms combinations, or mixtures easily taken for combinations, with various proportions of the hydroxide. It loses its water of crystallisation by heat, being at the same time partly decomposed, thus resembling the calcium salt. Anhydrous barium sulphide produced at temperatures below a red heat has not been described.

	Calculated.	Found.
Calcium	54·1	54·1
Sulphur	38·3	38·2
Hydroxyl.....	7·6	—
	100·0	

It is mentioned in the opening section of this paper that we have found ignited calcium sulphide less ready in forming hydrosulphide with hydrogen sulphide than lime itself. The cause of this evidently lies in the activity of the lime towards water, by which hydroxide is first formed. We are inclined to believe from our observations that calcium sulphide does not directly unite with hydrogen sulphide, but first changes to hydroxyhydrosulphide by taking up water.

Our attempt to form pure calcium sulphide by strongly igniting lime in a mixture of carbon dioxide and carbon bisulphide, following Schöne, gave us, after three hours' ignition, a mixture of 11CaS with 5CaO.* Air was excluded during the cooling. Sabatier also did not succeed by Schöne's method.

Hydrogen Sulphide decomposes Calcium Carbonate.

Carbon dioxide decomposes the calcium hydrosulphides. It would be needless to mention this, were it not that we have to call attention to the complementary reaction. We find that hydrogen sulphide decomposes calcium carbonate, so that in the precipitated form this salt becomes dissolved by hydrogen sulphide passed in a quick current through the water in which it is suspended.†

Carbon dioxide mixed with sufficient excess of hydrogen sulphide, may be sent through lime-water and yet not cause a precipitate,

* This symbolic expression, like analogous ones in other parts of this paper, means what it legitimately ought to do, according to the first principles of chemistry, 11CaS = 11 × 72 parts of calcium sulphide, and 5CaO = 5 × 56 parts of calcium oxide. The very prevalent custom of using symbols as mere abbreviations of names, without any quantitative signification, is much to be regretted in the interests of science. No doubt there will appear to many a justification for this practice, in its serving to distinguish two substances confused together under one name, between, for example, $[CO_2]$ and $[CO_3H_2]$, either of which is often called "carbonic acid." To those who feel this, I would propose the adoption of square brackets, as here just used, when formulæ are written as distinctive abbreviations. In any case, it would be better to avoid altogether the use of an ambiguous name like "carbonic acid," than to attempt to remedy confusion in nomenclature by confusion in notation.

† Barium carbonate in the precipitated state is slightly dissolved by hydrogen sulphide in the presence of much water (*Miller's Chemistry*), thus behaving like the calcium compound.

calcium hydrosulphide being formed. Here, then, is a case in which lime-water fails to detect the presence of carbon dioxide.

Hydrogen Sulphide decomposes Calcium Polysulphides.

Odling has pointed out, in his *Manual of Chemistry*, that hydrogen sulphide is liberated when a solution of calcium hydrosulphide is boiled with sulphur. Boiling alone will liberate hydrogen sulphide always, but with sulphur dissolving the evolution is greatly increased. We are able greatly to enlarge Odling's statement. Concentrated solutions of the hydrosulphide react with sulphur almost as energetically as hydrochloric acid solutions upon marble. To see this to advantage, the solutions of hydrosulphide should be a little warm, and the sulphur in powder. Ground roll is better than flowers, because it is free from acid and more easily moistened. The sulphur dissolves to an orange-red solution, and hydrogen sulphide escapes with very brisk effervescence.

Dissolution of sulphur in calcium hydrosulphide solution is attended with a distinct fall in temperature, as the following experiment shows. About 40 c.c. of a moderately strong solution contained in a deep tube surrounded with cotton-wool, was treated with powdered sulphur, and the mixture stirred with a thermometer. A fall of $2\frac{1}{2}^{\circ}$ C. was observed, namely from the temperature of the atmosphere, $26\frac{1}{2}^{\circ}$, to 24°.

By aiding the dissolution of the sulphur in the hydrosulphide by the heat of a water-bath until reaction ceases, that is, until the remaining sulphur stops effervescing with the solution and sinks to the bottom, the decomposition of the hydrosulphide becomes almost perfect, only a minute quantity remaining in the liquid. The calcium is converted, with the exception indicated, into pentasulphide.* When the decomposition is incomplete, all the calcium which is not hydrosulphide is pentasulphide. We would emphasise this statement, because Schöne (*Jahresb.*, **15**, 129; *Pogg. Ann.*, **117**, 58) has shown that when calcium monosulphide and sulphur are boiled in water together, there may be formed tetrasulphide as well as pentasulphide when the sulphur is not in excess. We find that although more than five atoms of sulphur to one of calcium may enter into solution during the reaction of sulphur upon the hydrosulphide (or the hydroxide), still when a pure pentasulphide solution has once cooled and deposited, as it does, the excess over five atoms, it cannot again be made to take up a perceptible quantity of additional sulphur by boiling this with it.

* Rose obtained barium polysulphide by heating solution of the hydrosulphide with sulphur, but evidently not under the condition of absence of hydroxide, and without this, that fact had not the special significance we find in the analogous one here described.

The reaction between calcium hydrosulphide and sulphur is made still more remarkable by being, as we have found it to be, reversible; that is, we find that hydrogen sulphide decomposes calcium pentasulphide readily, and, under suitable conditions, completely. Hydrogen sulphide bubbled through the pentasulphide solution produces a copious precipitate of pure sulphur, as freely as it would precipitate arsenic or selenium from solution. The calcium becomes hydrosulphide, and if the solution is cold and sufficiently dilute, all polysulphide is destroyed, as seen from the bleaching of the solution. In more concentrated solutions the conversion to hydrosulphide cannot be finished even in a freezing mixture. As when the reaction proceeds the other way, so here, the solution contains at any intermediate stage only hydrosulphide and pentasulphide.

We think these remarkable reactions may be attributed to the formation of hydrogen pentasulphide as a transition product. When hydrogen persulphide is dropped into a concentrated solution of calcium pentasulphide, it is resolved, with a strong effervescence such as a concentrated acid would cause, into hydrogen sulphide and sulphur. If now, with this "catalytic" decomposition in mind, we conceive in the reaction between calcium pentasulphide and hydrogen monosulphide, hydrogen pentasulphide to be constantly forming, and as constantly decomposing till the reaction is over, we may write for its formation—

$$CaS_5 + 2H_2S = CaS_2H_2 + H_2S_5;$$

and if, in the same way, hydrogen pentasulphide should be formed and decomposed continuously when calcium hydrosulphide and sulphur come into reaction, we may also write—

$$CaS_2H_2 + 8S = CaS_5 + H_2S_5,$$

and thus the matter becomes cleared up. To speak more generally, we have only to admit than when sulphur and hydrogen monosulphide meet, either one of them being free and the other in feeble combination, then hydrogen pentasulphide forms, and undergoes dissociation immediately afterwards.*

* Calcium pentasulphide is decomposed, by boiling its solution, into hydrogen sulphide, lime, and sulphur, a fact of which we have convinced ourselves by careful testing, although it had already been observed by others. We see in this evidence that calcium pentasulphide may be a hydroxyhydropentasulphide—

$$Ca\begin{matrix}S_5H\\OH\end{matrix},$$

and, in favour of this view, we may note that the only solid polysulphide of alkaline earth-metals known, barium and strontium tetrasulphides, contain water (Schöne). The division of the calcium between the weak sulphur acid and water is in accordance, too, with Berthelot's thermochemical views.

With this constitution of calcium pentasulphide adopted, a modification of the

We have still to give the essential details of our experiments. All along care was taken to keep air away from the solutions. The proof that sulphur can completely decompose calcium hydrosulphide was a qualitative one. Having heated the sulphur with the hydrosulphide just to the point when effervescence ceased, in a gentle current of hydrogen, maintained only to assist in keeping air out, the solution was cooled and then precipitated with manganese sulphate. The sulphur and manganous sulphide having been filtered off, the mother-liquor, relatively concentrated as it otherwise was, gave only a few flocks of precipitate—at first only a brown colour—with either copper or silver solution. Before adding these, however, the odour of hydrogen sulphide was quite distinct in it. We might have heated our pentasulphide solution a longer time than we did, probably with advantage, but we apprehended the decomposition of pentasulphide which hot water ultimately effects.

The evidence for the completeness of the decomposition of calcium pentasulphide by hydrogen sulphide was still more simple, and has been already mentioned, namely, the bleaching of the solution, a severe test, as will be admitted, when the great tinctorial power of alkaline polysulphides is remembered.

explanation given in the text is open to us of the remarkable reactions there described, as well as of the decomposition of the pentasulphide by water. The displacement of sulphur by water, and the displacements of sulphur and hydrogen sulphide, one by the other, are seemingly odd reactions, so to speak. Now if the pentasulphide is hydroxyhydropentasulphide, such displacements do not take place, and the reactions are then hardly peculiar in nature, thus—

$$CaOH(S_5H) + OH_2 = CaO_2H_2 + S_5H_2 (= 4S + SH_2)$$
$$CaOH(S_5H) + 2SH_2 = CaS_2H_2 + S_5H_2 + OH_2.$$

When sulphur is put into calcium hydrosulphide solution, it is also brought into contact with the products of the decomposition of the hydrosulphide with water. It then acts, not upon the hydrosulphide, but upon one of these products—the hydroxyhydrosulphide,—and by converting this into the pentasulphide, leaves room for a further decomposition of the hydrosulphide by water which, liberating more hydrogen sulphide, and again more, gives rise to the free escape of this gas. We need only formulate the first reaction, that between the sulphur and calcium hydroxyhydrosulphide:—

$$CaOH(SH) + 4S = CaOH(S_5H).$$

The nature of the reaction of hydrogen pentasulphide with calcium hydroxyhydropentasulphide is also more easy of interpretation than that of its reaction with the calcium pentasulphide. In the equation—

$$CaOH(S_5H) + S_5H_2 = CaS_2H_2 + 8S + OH_2,$$

two not improbable assumptions are made, one being that calcium hydroxide reacts with hydrogen pentasulphide, and the other that the di-pentahydrosulphide, $Ca(S_5H)_2$, dissociates to the hydrosulphide, and the thiosulphuric anhydride, $2S_4$ or $2SS_3$.

Quantitative tests were made to determine the composition of intermediate solutions. Solutions were prepared by boiling calcium hydrosulphide solution with sulphur, and then leaving them to cool, all in an atmosphere of hydrogen sulphide. One portion of solution for analysis was weighed out into zinc acetate solution and used for estimating the sulphur thus precipitated in the free state. The zinc sulphide was dissolved out with hydrochloric acid, and the free sulphur weighed, and tested for purity. Another quantity was weighed into potassium hydroxide, and oxidised by hypobromite. This was used for the estimation of the total sulphur and the calcium. Subtracting sulphur precipitated free by zinc acetate, from the total sulphur, gave us that precipitated as zinc sulphide. Subtracting from this a quantity chemically equivalent to the calcium, and dividing the remainder by 16, gave us the hydrogen combined with sulphur. The quantities of solution weighed out for analysis varied in amount from 1·615 grams to 0·810 gram.

First Preparation.—This was made from a solution of calcium hydrosulphide which had become a little yellow through atmospheric oxidation. In consequence of this, no doubt, the results of the analysis showed a slight deficiency in the sulphur of the polysulphide. They corresponded with the composition, calculated from the calcium, of $CaS_2H_2 + 3CaS_5$, but with about one-fourteenth part of the pentasulphide assumed to be changed into thiosulphate :—

	Calculated for $CaS_2H_2 + 3CaS_5$.	Found.
Calcium	10·47	(10·47)
Sulphur, precipitated combined ..	10·47	10·36
Sulphur, precipitated free	25·13	23·87
Sulphur, total	35·60	34·23

Second Preparation.—This gave results agreeing with the calculation for $25CaS_2H_2 + 22CaS_5$:—

	Calculated.	Found.
Calcium	7·57	(7·57)
Sulphur, precipitated combined ..	9·28	9·35
Sulphur, precipitated free	11·34	11·45
Sulphur, total	20·62	20·80

The Formation of Calcium Thiosulphate.

The conversion of calcium hydrosulphide into thiosulphate by oxidation is not uncommonly represented by the equation—

$$CaS_2H_2 + 2O_2 = CaS_2O_3 + OH_2,$$

but the correctness of this is more than doubtful.

Calcium hydrosulphide, as already described, undergoes saponification, or change into acid and base, to an extent limited only by the non-removal, as formed, of the hydrosulphuric acid. Calcium hydroxyhydrosulphide is an intermediate product, unless much water is present, and saponification proceeds more and more slowly in consequence of the formation of this less soluble salt, though it is not thereby arrested. When freely exposed to the air, the hydrosulphide, both in the solid state and in solution, rapidly and visibly changes so far as to lose half its sulphur as hydrogen sulphide, and by the time that this has happened very little thiosulphate has formed. Oxidation does not become considerable even during the conversion of the calcium to hydroxide and carbonate, provided that contact with fresh air is maintained. In illustration of the slowness of the oxidation, we may describe some experiments other than those referred to in previous sections.

For six hours we passed moist air deprived of its carbon dioxide in a rapid stream through a small volume of solution of calcium hydrosulphide, thus bringing the solution in contact with an enormous excess of fresh air. Very much hydroxyhydrosulphide (and hydroxide) separated out, but the quantities of thiosulphate and pentasulphide were so small that we did not proceed with their exact estimation.*

Another experiment was made simultaneously with the other, and like it, except for the modification of adding calcium hydroxide in order to convert as much as possible of the hydrosulphide at once to hydroxyhydrosulphide. It gave essentially the same results as the other, and certainly did not show greater oxidation. From this it will be seen that the evidence of the occurrence of material oxidation in the case of the basic salt is no stronger than in that of the normal salt. In order to get the formation of any considerable quantity of thiosulphate, the hydrosulphide or hydroxyhydrosulphide must be preserved in a limited space, the atmosphere in which can only slowly renew itself.

All the experiments we have made fairly lead us to the conclusion that it is hydrogen sulphide which oxidises, and then, by its products reacting with the hydroxyhydrosulphide, forms the thiosulphate. The oxidation of hydrogen sulphide, though slow, is probably not more so, under favourable circumstances, than the formation of thiosulphate, well known to be slow, and is here no doubt quickened by the influence

* After adding zinc acetate solution, the filtrate from the very large precipitate, scarcely diluted with washings, gave with barium chloride and bromine only a very slight precipitate on heating. The zinc precipitate was partly (apparently more than half) soluble in acetic acid and in hydrochloric acid, left only a small amount of flocculent sulphur.

of the basic substance—calcium hydroxyhydrosulphide. The equation—

$$Ca\begin{matrix}SH\\OH\end{matrix} + 2O_2 + SH_2 = Ca\begin{matrix}S\\O\end{matrix}SO_2 + OH_2,$$

probably gives a correct view of the reaction, so far as it is yet understood. Here we may remark that, from the point of view of the constitution of a thiosulphate, the equation $CaS_2H_2 + 2O_2 = CaS_2O_3 + OH_2$ is not easy to follow.

Of the occurrence of oxidation of the hydrogen sulphide with the formation of sulphur, there is the strongest evidence in the considerable production of calcium pentasulphide from the very commencement of the oxidation. Any explanation of the production of thiosulphate is insufficient that leaves out of consideration the simultaneous production of pentasulphide. The latter has received a separate explanation in which the sulphur necessary to combine with calcium monosulphide is derived from the oxidation of another part of the calcium sulphide, into lime and sulphur: the soundness of the form of oxidation here assumed to take place can hardly be sustained. Calcium sulphide when dry does not oxidise at common temperatures, and when heated it oxidises to sulphite and sulphate. When moist it only slowly yields oxidation-products, and then not without hydrolysis into hydrogen sulphide and lime. Calcium sulphide does not combine with sulphur even when heated with it, if dry, and if moist only by previous hydrolysis also, and actual escape of hydrogen sulphide.

The lixiviation of soda-waste, and especially that carried on experimentally by Kraushaar, serves to show that with a very limited supply of air, the oxidation of the hydrogen sulphide, which we hold to take place, yields unoxidised sulphur which then forms polysulphide, while a further admission of air produces oxidised sulphur for the production of thiosulphate.

The fact that pentasulphide always accompanies thiosulphate, suggests the question whether the formation of pentasulphide precedes and leads to that of thiosulphate. We have tested the point to some extent by experiments, without getting decisive results; but it seems to us more probable from them than not, that the formation of thiosulphate does not depend upon that of pentasulphide.

We thought it worth testing whether atmospheric oxidation might possibly be essential to the production of pentasulphide and thiosulphate when sulphur and lime are boiled together in water, and found that this reaction went on just as well in an atmosphere of coal-gas as in air. Lime and sulphur seem to be without distinct action upon each other in cold water.

We tried the effect of lime upon calcium pentasulphide. In the

cold no thiosulphate was formed in a day. When the two substances were boiled together, with exclusion of air, a very slight formation of thiosulphate occurred, but this fact has no significance, because the pentasulphide by itself very slowly yields thiosulphate in a boiling solution. Whether the nascent sulphur of oxidising hydrogen sulphide can act upon lime in the cold, in the same way as free sulphur acts upon it in boiling water, we cannot tell.

Calcium pentasulphide is stated to yield thiosulphate both by reaction with water and with the oxygen of the air. Schöne observed that potassium pentasulphide boiled with water yielded a little thiosulphate. By long boiling of calcium pentasulphide solution out of contact with air, very small quantities only of thiosulphate are formed, provided evaporation does not proceed so far as to cause the separation of much solid matter. When, however, the solution is boiled down until much sulphur and lime have separated out (and hydrogen sulphide escaped), a not inconsiderable amount of thiosulphate is produced. We do not think that these experiments, or those of Schöne, prove that any direct conversion of pentasulphide into thiosulphate by water takes place:—

$$CaS_5 + 3OH_2 = CaS_2O_3 + 3SH_2$$

(*Watts's Dict.*, 1st Suppl., p. 957), for after lime and sulphur have separated out these substances can react to form thiosulphate in the known way, and before they have done so to a visible extent the minute quantities of thiosulphate found may arise from a slight entrance of air, or even from a slight formation of lime and sulphur at the surface or edges of the liquid. To accept the above equation is to admit that water can oxidise sulphur like the oxide of a metal.

As is well known, calcium pentasulphide by the action of the air yields sulphur and calcium thiosulphate. From experiments which we have made, the change that occurs would seem to be not so simple as is supposed. A wide-mouthed glass jar of about 26 litres' capacity was prepared by placing some fully slaked lime in it in a thin layer over the bottom, and leaving it tightly closed up for a day in order to remove carbon dioxide from the enclosed air. Then it was opened, a watch-glass holding pure concentrated solution of pentasulphide quickly inserted, and the cover replaced. In a day the solution had crusted over. The bottle was again opened, and the air in it tested and found still to contain much oxygen. This air was, however, partly replaced by oxygen-gas, for fear that it might not in itself contain enough. The bottle was reclosed and left for six days more, and then finally opened. The air within could still rekindle a glowing taper. The pentasulphide solution was still yellow and clear, but had a thick crust on its surface. There was no odour observable in

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the bottle, and the lime showed no sign of discoloration on its surface. Throughout the experiment there was condensed water on the walls of the bottle, and no sensible loss in volume by the solution was noticeable. The crust on the solution was found to be sulphur, neither carbonate nor other calcium salt being found in it. The solution, in spite of its yellow colour, contained very little sulphide, and nothing else but a very great abundance of thiosulphate.

Some solution of pentasulphide exposed to the air in a watch-glass gave essentially the same result, but, in the first place, it dried up in a few days (when the water was renewed and again dried up in a few more days); in the second place, all sulphide was decomposed; and, in the third place, much calcium carbonate was found with the sulphur, and the thiosulphate was not so abundant as in the exposure in the bottle. Some solution of pentasulphide was also exposed to the air in a watch-glass, but mixed with lime, and gave results the same as before, except that a very little sulphide had escaped change, and that the solution reacted strongly alkaline from the presence of lime.

These experiments are in entire conformity with the requirements of the equation—

$$CaS_5 + 3O = CaS_2O_3 + 3S,$$

and we should have described them more briefly but for the result of another form of the experiment. We passed for several hours a rapid stream of air deprived of its carbon dioxide through a small quantity of pentasulphide solution, and found that the air was always carrying away with it small quantities of hydrogen sulphide, and that the solution gradually deposited crystals of sulphur and of Schöne's hydroxytetrasulphide of calcium, a compound of hydroxide with tetrasulphide of calcium. As when boiled, therefore, saponification of some of the pentasulphide had occurred, and then the lime had decomposed some more pentasulphide into sulphur and tetrasulphide, and combined with the latter. We treated the whole with zinc acetate and tested for thiosulphate as usual. We found no more thiosulphate apparently than the minute quantity we had found the solution to contain before treatment—that is to say, we found that either no thiosulphate at all, or as we prefer to put it, only a trace had been produced.

We cannot but regard this experiment as a proof that direct oxidation of pentasulphide by the air does not happen, and that the oxidation is that of hydrogen sulphide. Hydrogen sulphide is slowly liberated from the pentasulphide, and if this is rapidly removed as it forms, the remaining penta- and tetra-sulphides undergo no oxidation by free oxygen. When solution and air are left in contact at rest,

the oxidation of the hydrogen sulphide keeps pace with its liberation, and its oxidised products then react upon the pentasulphide to form thiosulphate and sulphur. We may suppose the reaction with water to be that expressed by—

$$CaS_5 + 2OH_2 = Ca\begin{matrix}SH\\OH\end{matrix} + 3S + SH_2,$$

and then with oxygen, as before represented—

$$Ca\begin{matrix}SH\\OH\end{matrix} + 2O_2 + SH_2 = Ca\begin{matrix}S\\O\end{matrix}SO_2 + 2OH_2.$$

XLI.—*Contributions to the History of the Naphthalene Series. β-Naphthaquinone.* Part II.

By Charles E. Groves, F.R.S.

In a short preliminary note published in the *Chemical News* (**45**, 267) some time ago, on the preparation of β-naphthaquinone from "β-naphthol orange," as proposed by Liebermann (*Ber.*, **14**, 131; *Annalen*, **211**, 51), I pointed out the disadvantages of this method as compared with that originally described by Stenhouse and myself, and I now purpose to lay before the Society a detailed account of the experiments, and also some further contributions to the history of β-naphthaquinone and its derivatives.

Preparation of β-Naphthaquinone from β-Naphthol Orange.

In the communications referred to above, Liebermann recommends the sodium salt of β-naphthol-diazobenzene-sulphonic acid,

$$OH.C_{10}H_6.N_2.C_6H_4.SO_3H,$$

known commercially as "β-naphthol orange," as the best material from which to prepare β-naphthaquinone. The process consists in treating the β-orange with hydrochloric acid and stannous chloride in excess, so as to decompose it and convert it into a mixture of para-amidobenzenesulphonic acid with the stannochloride* of amido-β-naphthol. The amido-β-naphthol is then separated from this mixture by dissolving it in water, precipitating the tin by hydrogen sulphide,

* It is preferable to use the term *stannochloride*, instead of "*double tin salt*," for compounds of the formula $RCl,SnCl_2$, &c., in the same way that "platino-chloride" is now almost universally substituted for "double platinum salt."

separating the stannous sulphide by filtration, and evaporating in a current of hydrogen sulphide to remove excess of hydrochloric acid; the crystalline mixture of amido-β-naphthol hydrochloride with sulphanilic acid is then treated with a concentrated solution of sodium carbonate, and the free amido-β-naphthol extracted by agitation with ether, of which large quantities are required, as the base is but sparingly soluble in it. On distilling off the ether, the base is left in the crystalline state, and is then converted into sulphate and oxidised to β-naphthaquinone in the manner described by Stenhouse and myself (*Chem. Soc. J.*, 1877, ii, 47, and Trans., 1878, 415). As it seemed to me that this method of obtaining the amido-β-naphthol sulphate was very troublesome and tedious, I carefully repeated Liebermann's experiments, and although I can confirm his statements as to the results, I must dissent from his opinion that the process affords a convenient means of preparing β-naphthaquinone in quantity. The decomposition of the stannochloride by hydrogen sulphide, and the subsequent evaporations, extraction with ether, &c., render the process unwieldy when any considerable quantity of material is operated on, quite irrespective of the unavoidable loss of ether. If, on the other hand, we attempt to precipitate the β-naphthaquinone from the solution directly by an oxidising agent, without first separating the sulphanilic acid, the product is unsatisfactory, both in quantity and in quality, whether the tin has been removed by precipitation with hydrogen sulphide or with zinc.

It was evident that in order to render Liebermann's process at all workable, some means must be devised to obviate the treatment with hydrogen sulphide, and to separate the regenerated sulphanilic acid without resorting to agitation with ether, &c. A few preliminary experiments showed that these difficulties could be overcome, the first by avoiding the use of the large excess of stannous chloride recommended by Liebermann, and the second by removing the sulphanilic acid as sodium salt. When β-naphthol orange is heated with stannous chloride and hydrochloric acid in slight excess over that required by the equation $OH.C_{10}H_6.N_2.C_6H_4.SO_3Na + 2SnCl_2 + 6HCl = OH.C_{10}H_6.NH_2,HCl + NH_2.C_6H_4.SO_3H + 2SnCl_4 + NaCl$, the diazo-compound is completely decomposed, and, on cooling, the amido-β-naphthol crystallises out, not as stannochloride, but as hydrochloride, mixed of course with sulphanilic acid; in this way the amount of stannous chloride is reduced by 50 per cent., and the necessity for precipitating large quantities of tin as sulphide is avoided.

A mixture of 100 c.c. of stannous chloride solution (containing 40 grams of tin) with 110 c.c. of hydrochloric acid, sp. gr. 1·16, is poured on to 60 grams of the β-orange in a flask and well shaken; reduction takes place rapidly, and in about 10 minutes' time the mix-

ture becomes of a pale pink colour; 300 c.c. of boiling water is then added, and the whole boiled for a few minutes, when the product dissolves, all but a little black tar which can be separated by filtering hot, best through a vacuum filter. As the liquid cools, a mixture of amido-β-naphthol hydrochloride with sulphanilic acid separates, whilst the tin remains in solution as stannic chloride, and may be separated by filtration. On concentrating these mother-liquors and adding strong hydrochloric acid, the remainder of the amido-compound may be recovered as hydrochloride, this being almost insoluble in strong hydrochloric acid.

In order to effect the separation of the base from the sulphanilic acid, the mixture is treated with sodic hydroxide in quantity sufficient not only to combine with the sulphanilic acid, but also to set free the amido-β-naphthol from its hydrochloride. As the free base is almost insoluble in water, the sodium sulphanilate and chloride are easily washed out, and the free base can then be converted into hydrochloride or sulphate. The process is carried out as follows:—The crystalline product from 60 grams of the β-orange is collected, dissolved in 180 c.c. boiling water, and cooled quickly with agitation, so as to deposit the mixed sulphanilic acid and amido-hydrochloride in a finely divided state; 20 c.c. of a normal soda-solution (containing 40 grams NaHO in 100 c.c.) are then added with constant stirring, and after 10 minutes, 10 grams of hydrogen sodium carbonate, the object of this being to convert the excess of sodium hydroxide into carbonate. The mixture is occasionally stirred, and after the lapse of another 10 minutes, the free amido-β-naphthol is collected on a vacuum-filter and washed with 180 c.c. water, which has been partly saturated with hydrogen sulphide, to prevent the free base from becoming oxidised during the washing; the treatment with soda and subsequent collection and washing being conducted as rapidly as possible to avoid loss by oxidation. In this way the sulphanilic acid is removed as sodium salt, and may be recovered from the filtrate by evaporating it and precipitating with hydrochloric acid. The moist amido-base may at once be converted into hydrochloride by boiling it with 200 c.c. water and 12·5 c.c. of concentrated hydrochloric acid. The yield of crystallised amido-β-naphthol hydrochloride obtained by these means is from 35—39 per cent. of the weight of the β-orange. This agrees very nearly with the result obtained by Liebermann (38 per cent.) by the troublesome process of decomposing the stannochloride with hydrogen sulphide, extracting the base by agitation with ether, and subsequently converting it into the hydrochloride.

From the results formerly obtained with nitroso-β-naphthol*, it

* I have retained the name *nitroso-β-naphthol* in this paper, for although I am

seemed possible that ammonium or sodium sulphide might be employed for reducing the diazo-compound, and that this, on the small scale, would have an obvious advantage over the stannous chloride method, inasmuch as the sulphanilic acid would remain in solution as ammonium or sodium salt. The following was found to be the most advantageous mode of carrying out the process:—2 parts of the β-naphthol orange are dissolved by boiling in 1 part of the normal soda-solution above-mentioned diluted with 6 of water, and a rapid current of hydrogen sulphide is passed through the hot solution. At first the gas is absorbed without any apparent change, but soon the free base begins to separate in lustrous plates, and the brilliant red solution becomes of a dingy brown. The crystals rapidly increase in number, and after a time, when the red colour has entirely disappeared and the gas is no longer absorbed by the yellow solution of sodium polysulphide, the flask is tightly corked, allowed to remain for 18—20 hours, and then again saturated in the cold with hydrogen sulphide. The object of this second treatment with hydrogen sulphide is to precipitate the last portions of amido-naphthol, as it is insoluble in solutions of sodium sulphide saturated with hydrogen sulphide, although it is readily soluble if any free alkali is present.

The free base, which is mixed with more or less sulphur, but is quite free from sulphanilic acid, is collected on a vacuum filter, and washed with 200 c.c. dilute hydrogen sulphide solution, to remove the sodium sulphide and sodium sulphanilate; it may then be converted into the hydrochloride in the manner already described, using the same proportions of hydrochloric acid and water. The yield of hydrochloride is from 35—37 per cent. of the weight of the β-orange. If the experiment of reducing the β-orange with hydrogen sulphide is made on a small scale—10 to 15 grams—it is advisable to keep the vessel hot by immersing it in a water-bath, at all events until the free base begins to crystallise out; with larger quantities, however, this is unnecessary, as the heat developed during the reaction is sufficient to maintain the temperature. The reduction may also be effected by passing hydrogen sulphide into the β-orange mixed with aqueous ammonia, but it is less convenient, for the reaction does not take place as readily as with sodium hydrogen sulphide; moreover, the volatility of the ammonium sulphide is an objection.

Preparation of Amido-β-Naphthol from Nitroso-β-Naphthol.

Nitroso-β-Naphthol.—In a former paper (*Chem. Soc. J.*, 1877, ii, 47) a method was given for preparing nitroso-β-naphthol, which

inclined to regard it as belonging to the class of hydroximido- or isonitroso-compounds, the evidence we have as to its constitution is inconclusive at present.

yielded very satisfactory results. At the present time, nearly pure sodium nitrite is made on the large scale for use in the coal-tar colour industry, and it would obviously be an advantage if a commercial article like this could be employed, instead of nitrosyl sulphate which has to be made in the laboratory. A few preliminary trials rendered it evident that nitroso-β-naphthol might be prepared by this means with the greatest ease, even on the large scale. A solution of sodium β-naphthol and sodium nitrite is first made by boiling 4 parts of β-naphthol with 3 parts by measure of the normal soda-solution and 8 parts of water, until the naphthol has completely dissolved, and adding it to a solution of 3 parts of sodium nitrite in 300 of cold water. This solution is then poured, with constant stirring, into 5 parts by measure of sulphuric acid, diluted with 2000 of water; the mixture assumes a deep orange colour, then a black tarry scum separates on the surface, but on continuing to stir for a few minutes, the deep yellow nitroso-compound is formed, and the scum disappears. The mixture is stirred occasionally during the next hour or so, and then allowed to remain until the next day, when the crude nitroso-β-naphthol may be collected, and washed with a little water. In order to purify it, the moist paste is made up to 140 parts with water, mixed with 4 parts normal soda-solution previously diluted with 140 of water, and filtered (on the large scale it is better to employ a Taylor's bag filter with a head of 6—8 feet of the liquid). It is important to dissolve the crude product precisely in the manner described, as if concentrated soda-solution is added to the mixture, more or less of the green crystalline sodium-derivative of nitroso-β-naphthol is at once precipitated, and dissolves again with great difficulty; this does not occur if the soda-solution is dilute. The clear filtrate (280 parts) containing sodium nitroso-β-naphthol is then mixed with 16 parts of the normal soda-solution; this throws down the sodium-derivative as a bright green crystalline powder, as it is but very sparingly soluble in solutions containing free sodium hydroxide. The green precipitate is collected, and if necessary purified by washing it with dilute soda-solution (4 parts of the normal solution to 40 of water). When decomposed by dilute hydrochloric acid, it yields nearly pure nitroso-β-naphthol, which may be further purified by crystallisation in the manner previously described (*loc. cit.*).

In dissolving the crude nitroso-derivative in soda-solution, it is advisable to use ordinary river or well water, as the small quantity of insoluble calcium nitroso-β-naphthol formed greatly facilitates the filtration; when considerable quantities are operated on, it is worth while to recover this from the insoluble residue by treating it with dilute hydrochloric acid at the ordinary temperature for a day or two, washing until nearly free from acid, and extracting the nitroso-

naphthol with very dilute soda-solution. It may then be precipitated by acid and purified along with a fresh batch of the crude nitroso.

Amido-β-naphthol Hydrochloride, $OH.C_{10}H_6.NH_3Cl$. — This may be prepared from the sodium-derivative of nitroso-β-naphthol, by reducing it with ammonium or sodium sulphide in the same way as described for the β-orange. The sodium salt from 1 part β-naphthol is mixed with 8 of water, a little ammonia or soda-solution added, and a slow current of hydrogen sulphide is passed into it, heating gently to about 40°, at first, to start the reaction; when the liquid is nearly saturated with the gas, the temperature is raised to 100°, and the rest of the operation conducted precisely as in the case of the diazo-compound. This method, although very convenient for obtaining small quantities of the free base, is not adapted for the preparation of the hydrochloride on the large scale, firstly, owing to the large quantities of hydrogen sulphide required, and secondly, the product is almost always more or less coloured, apparently by the product of a secondary reaction between the free amido-base and the nitroso-derivative in alkaline solution. On the small scale, however, the base is obtained in almost colourless crystals.

When the hydrochloride is required in quantity, the best method is to act on the sodium nitroso-naphthol with hydrochloric acid and stannous chloride, using sufficient merely to reduce it to the amido-derivative without forming the stannochloride. For this purpose it is unnecessary to prepare the nitroso-naphthol from its sodium-derivative; in fact, the latter being a somewhat dense crystalline powder, is far more convenient to operate upon than the felted mass of fine needles in which the free nitroso-compound separates from its metallic derivatives. The moist sodium-derivative from 4 parts β-naphthol, prepared in the manner already described, is made up with water until the bulk is 80 parts, and the thin creamy liquid thus obtained is poured in a slender stream with constant stirring into a mixture of 15 parts by measure of hydrochloric acid, sp. gr. 1·16, with 14 of a solution of stannous chloride (100 c.c. = 40 grams Sn) in a capacious beaker. The first portions dissolve completely, the solution acquiring a brownish tint; but as more of the sodium salt is added, white crystals begin to form, the mixture becomes warm, and the sodium salt is reduced and converted into the amido-naphthol hydrochloride, as fast as it comes in contact with the acid solution. Care must be taken, however, to add the solution gradually and with constant stirring, otherwise dark-coloured secondary products will be formed, which are very difficult to remove. The mixture is left to itself for an hour with occasional stirring, and the beaker is then heated in the water-bath until the crystals are dissolved, and nothing but a small quantity of a dark-coloured flocculent substance is left

suspended in the liquid; owing to its mucilaginous nature, it is, however, practically impossible to remove this by filtering the *hot* solution, and a somewhat indirect method of separating it has to be adopted. The hot solution is therefore allowed to cool slowly; next day a cake of crystals will be found at the bottom of the beaker resting on the finely divided impurities; the supernatant clear liquid is then syphoned or poured off, and the crystals are freed from the impurities by elutriation, using for this purpose successive quantities of the clear liquid which has been poured off; when the washings are clear, the crystals of amido-naphthol hydrochloride may be collected. A large proportion of the substance, however, still remains in solution; this is filtered, concentrated by evaporation, and the crystals are collected and washed with dilute hydrochloric acid, in which they are almost insoluble. The yield of crude amido-hydrochloride is from 100 to 105 per cent. of the weight of the β-naphthol originally employed. As it oxidises somewhat rapidly when exposed to the air in the moist state, it should either be at once converted into β-naphthaquinone, or preserved under a dilute aqueous solution of sulphur dioxide in a well closed bottle nearly filled with the substance. If the pure hydrochloride is carefully dried at 100°, and introduced into a well stoppered bottle while hot, it may be preserved without undergoing oxidation, but heat appears to have caused some change, as the β-naphthaquinone prepared from it is dark coloured; this impurity is removed by recrystallisation from water, but is again formed on drying the crystals at 100°.

In order to purify the amido-β-naphthol hydrochloride, it is dissolved in 8 parts of boiling water, a little sulphurous acid solution added, the liquid is filtered, and to the boiling filtrate is added about 5 per cent. of its bulk of strong hydrochloric acid. As the hydrochloride is but sparingly soluble in dilute hydrochloric acid, the greater part separates in the crystalline state as the solution cools; that which remains dissolved may be recovered by boiling the solution down rapidly without access of air. The hydrochloride is much less soluble in cold than in hot water, and requires nearly 15 parts of boiling spirit to dissolve it.

When the hydrochloride of the base is oxidised by passing a current of air through its cold aqueous solution (1 part in 40 of water) by means of an aspirator, a bluish-black substance is formed, which is insoluble in hydrochloric acid, but dissolves in cencentrated sulphuric acid with blue colour, and is reprecipitated on adding water to the solution. It is oxidised by nitric acid and by chromic mixture, but without formation of β-naphthaquinone, and when treated with alcoholic stannous chloride, it is reduced and dissolved. The nature of this substance has not as yet been investigated.

Amido-β-naphthol sulphate, formed by dissolving the base in warm

dilute sulphuric acid crystallises easily, but is less soluble than the hydrochloride. The base does not seem to form salts with acetic or oxalic acid.

β-Naphthaquinone.

Details of a method for preparing β-naphthaquinone by the oxidation of amido-β-naphthol sulphate with dilute chromic mixture were given in a former paper (Trans., 1878, 415), but I find it is more advantageous to employ ferric chloride, as this may be used in excess and left for some time in contact with the precipitate without causing any change; whereas with chromic mixture the quinone is attacked, and soon becomes contaminated with brown amorphous products.

The best method of proceeding is as follows:—1 part of powdered amido-β-naphthol hydrochloride is placed in a flask, 2 parts of a saturated solution of sulphur dioxide is added, and then 40 parts of boiling water; the mixture is agitated until the hydrochloride is entirely dissolved, and the flask is then corked and left to cool. When cold, the solution is filtered from the small quantity of undissolved impurity, and the clear filtrate poured at once into 12 to 14 parts of a solution of ferric chloride (100 c.c. = 10 grams Fe_2O_3). The mixture becomes momentarily darker in colour, and immediately afterwards deposits the β-naphthaquinone in orange-yellow microscopic needles. After the lapse of half an hour the quinone is collected on a vacuum-filter, and must be carefully washed to remove the iron salts and free acid; this is best done by removing the precipitate from the filter, stirring it up thoroughly with 20 parts water, allowing it to remain for 20 minutes with occasional stirring, and again collecting; repeating the washing a second time in the same way, and finally drying the product at a gentle heat in an atmosphere free from acid fumes. The quinone obtained in this way is pure and of a deep golden colour. The yield is from 70—72 per cent. of the weight of the hydrochloride taken, or 73—75 on the β-naphthol originally employed.

Now, as the commercial value of β-naphthol is not more than half that of β-naphthol orange, and as the former yields 100 parts quinone for 40 obtained from an equal weight of the β-orange, it follows that to produce a given quantity of β-naphthaquinone by Liebermann's process, the cost for raw material will be at least five times as great as by the one just described, and what is of far more importance in the laboratory, the latter method is comparatively simple and involves but little trouble.

The reaction in this case may be thus expressed:—

$$OH.C_{10}H_6.NH_3Cl + Fe_2Cl_6 + OH_2 = C_{10}H_6O_2 + 2FeCl_2 + NH_4Cl + 2HCl.$$

The amount of ammonic and ferrous salts found in the solution after reaction is sensibly that required by the above equation. There can be but little doubt, however, that under the influence of the oxidising agent the NH_2-group is first replaced by OH, thus:—

$$OH.C_{10}H_6.NH_3Cl + OH_2 = OH.C_{10}H_6.OH + NH_4Cl,$$

and that the quinol is immediately oxidised to the quinone. The reaction is analogous to that which I observed to take place when trichlororcinol, $C_6MeCl_3(OH)_2$, is treated with an oxidising agent in alkaline solution, one of the chlorine atoms being replaced by OH and the quinol oxidised to the quinone, $C_6MeCl_2(OH)O_2$. The conversion of trichlorophenol into dichloroquinone by nitric acid is another instance of the same kind.

Nitro-β-Naphthaquinol.

In a former paper (Trans., 1878, 416) the preparation and properties of nitro-β-naphthaquinone were fully described, and it was mentioned that two compounds were obtained from it by the reducing action of hydriodic acid and phosphorus—apparently nitro-β-naphthaquinol and amido-β-naphthaquinol. Since then I have more carefully examined these two substances, which may be conveniently prepared by employing stannous chloride as the reducing agent; the nitroquinol being obtained with a cold dilute solution of the tin salt, whilst the more energetic action of a hot concentrated solution converts the nitro- into an amido-group.

In preparing nitro-β-naphthaquinol, $C_{10}H_5(NO_2)(OH)_2$, 10 parts of β-naphthaquinone are converted into the nitro-derivative, and the moist product (equal to 8 parts dry nitro-β-naphthaquinone) is mixed with 40 of water; on to this is poured 15 parts, by measure, of a solution of stannous chloride (100 c.c. = 40 grams Sn) previously mixed with 15 of concentrated hydrochloric acid and 80 of water. The liquid immediately becomes of a deep red from solution of part of the nitro-β-naphthaquinone, but in a few minutes it again becomes paler from separation of the quinol. It is allowed to remain for two hours with occasional stirring, then collected, washed with 40 parts water, in which it is almost insoluble, and dried. The nitro-quinol may be purified by crystallising it from acetic acid or alcohol, in which it is readily soluble, or from benzene. It separates from benzene and from alcohol in crimson rhomboidal plates, and from acetic acid in long prisms. The yield is from 80 to 90 per cent. of the β-naphthaquinone taken.

It is reconverted into nitro-β-napthaquinone by treatment with dilute chromic mixture, and warm dilute nitric acid has the same action, but if it is boiled with the acid for any length of time it is

oxidised to phthalic acid in the same way that naphthaquinone itself is, thus proving the NO_2-group to lie in the same ring as the quinonic $(O_2)''$-group. On adding ferric chloride solution to a warm alcoholic or acetic solution of the quinol, it is not reconverted into the quinone, but the red colour is at once changed to a yellowish-green, and the solution soon deposits *nitro-β-naphthaquinhydrone* in minute prisms; this compound is also formed by the action of an aqueous solution of ferric chloride on the quinol, but it is not produced on boiling an acetic or alcoholic solution containing the nitroquinol and nitroquinone in equal molecular proportions. The quinhydrone is of a dark bronze-green colour when dry: it is soluble in alcohol and in acetic acid, but only sparingly in ether, and almost insoluble in benzene.

Amido-β-Naphthaquinol.

β-Naphthaquinone may be converted into the amido-derivative by submitting it to the action of energetic reducing agents, such as tin and hydrochloric acid, or hot concentrated stannous chloride solution. It is far better, however, to convert it first into the nitro-β-naphthaquinol and to act on this with tin and hydrochloric acid. The moist nitro-quinol from 10 parts of β-naphthaquinone, prepared in the manner just described, is placed in a capacious beaker with 15 parts of finely divided tin (such as is obtained by precipitation with zinc) and 40 of concentrated hydrochloric acid is poured on to it. The beaker is now immersed in boiling water and well stirred, when a violent reaction sets in, which, unless the quantity operated on is small, must be moderated by removing the beaker and plunging it into cold water. In a very short time the red colour entirely disappears, and the reaction is completed. When cold, the crystals are collected and purified by recrystallisation from hot water, in which they are easily soluble. The *amido-β-naphthaquinol hydrochloride*, $C_{10}H_5(OH)_2.NH_3Cl$, forms large pale yellow crystals, which, like those of amido-β-naphthol hydrochloride, are rapidly oxidised on exposure to the air.

In conclusion, I wish to draw attention to the fact that, although in a paper published in conjunction with the late Dr. Stenhouse, I mentioned the production of amido-β-naphthaquinone by the action of reducing agents (*Annalen*, **194**, 203), and in a notice in the *Berichte*, (**14**, 1659), especially addressed to Prof. Liebermann, I stated that I was engaged in an investigation "of nitro-β-naphthaquinone and the products obtained from it by the action of reducing agents," a student in the "örg Laboratorium d. tech. Hochschule," working under Prof. Liebermann's direction, has recently published a note in which he describes the reduction of nitro-β-naphthaquinone to amido-β-naphthaquinone without the slightest reference to its having been already done.

XLII.—*On a Bye-product of the Manufacture of Aurin.* Part II.

By Adolf Staub, Ph D., and Watson Smith, Lecturer on Technical Chemistry in the Owens College, Manchester.

In a former paper by Alexandre Claparède and one of us (this Journal, August, 1883), it was shown that the bye-product referred to is formed by the direct union of 2 mols. of phenol with 1 of anhydrous oxalic acid. In a new experiment, by repeated recrystallisation from pure glacial acetic acid, and after drying in a vacuum over calcium chloride and quicklime, the crystals were obtained in a perfectly pure state, as the following analysis shows:—

0·4215 gram of substance gave on combustion 0·9280 gram CO_2, and 0·1915 gram H_2O.

	Calculated for $C_{14}H_{14}O_6$.	Found.
C	60·40 per cent.	60·05 per cent.
H	5·03 „	5·05 „

As already stated, this compound may be considered as the phenyl-ortho-oxalic ether, which view is supported on the one hand by the instability of the substance, and on the other by the fact that the two naphthols form compounds analogous to it, though somewhat less readily. The experiment has also been tried with resorcinol, but up to the present time no success has attended our efforts to isolate any analogous compounds. We had entertained some hopes of being able to obtain either a compound in which 1 mol. of anhydrous oxalic acid unites with 2 of resorcinol, or one in which 1 mol. of oxalic acid is combined with 1 of resorcinol, both hydroxyl-groups of the resorcinol molecule in the latter case being engaged. All hope in this direction has not yet been abandoned, and should it be realised we shall have important evidence of the so-called water of crystallisation of oxalic acid, existing in a form of union in the oxalic acid molecule, somewhat closer than water of crystallisation is usually believed to exist in—the evidence, in short, being in favour of crystallised oxalic acid being an ortho-acid, and being formulated—

$$\begin{matrix} HO.C(OH)_2 \\ | \\ HO.C(OH)_2 \end{matrix} \quad \text{rather than} \quad \begin{matrix} CO.OH \\ | \\ CO.OH \end{matrix} + 2H_2O.$$

The melting point of the phenyl ortho-oxalate, as determined in a capillary tube, was found to be 126—127°. It was altered by the presence of the smallest trace of moisture, and can be exactly deter-

mined only by using the greatest care. By heating the substance in sealed tubes for five hours at about 180°, it was completely decomposed, yielding phenol, carbonic oxide, carbon dioxide, and water. On heating it with concentrated sulphuric acid for some time at 100—120°, aurin is obtained.

To test the result of this reaction in presence of free phenol, 18 grams of the phenyl ortho-oxalate were mixed with 7 grams of phenol and 10 grams of pure concentrated sulphuric acid, and the mixture was heated for about 20 to 22 hours at 120—125°. The melt was poured into water, and the mixture boiled for some time to remove phenol and other soluble products. After boiling twice, crude aurin was left in a fairly pure state, and only 9 grams of the crude substance were thus obtained from 18 grams of the bye-product.

This small yield of aurin makes it probable that the presence of free phenol does not increase the formation of aurin. That it was aurin was proved by the crimson-red colour of the alkaline solution, and the reaction of the latter solution with acids in excess. After standing for 24 hours, the aqueous solution was filtered off, and treated with barium carbonate in order to remove free sulphuric acid. By evaporation of the filtered solution, 23 grams of barium paraphenolsulphonate crystallised out in small white needles.

0·745 gram of substance gave 0·3387 gram of barium sulphate.

	Calculated for $(OH.C_6H_4.SO_3)_2Ba + 3H_2O$.	Found.
Ba	25·51 per cent.	25·65 per cent.

During the above-mentioned process of heating the bye-product with phenol and sulphuric acid, the gases evolved during the reaction were caused to pass through water, and on testing this solution only traces of formic acid were detected. This result consequently does not bear out the theory involved in the equation expressing the formation of aurin in the former paper (Part I, this Journal, Trans., 1883, p. 358), in which it appears that formic acid should be generated. To investigate this question more closely, a quantity of pure potassium phenolsulphonate (one of a series of fine preparations manufactured by Messrs. Charles Lowe and Co.) was mixed with the calculated proportions of anhydrous oxalic acid and concentrated sulphuric acid, and heated as in the usual way in the preparation of aurin. It was then found that if during any stage of the process, the melt was allowed to cool, instead of the abundant sublimation of ortho-phenyl oxalate, only a few stray crystals of this compound were discernible, and this quite out of proportion in amount to what is found in the usual process of aurin preparation. The result thus obtained indicates that the ortho-phenyl oxalate plays no part as an intermediate product in the forma-

tion of aurin. The following experiment shows clearly how the substance may be formed during the process of the manufacture of aurin. Vapours of phenol were passed into a dry flask in which oxalic acid was being sublimed; an abundant deposit of the crystals of the orthophenyloxalate was formed on the cooler portions of the interior of the flask. These results, then, coincide best with the theory expressed in Nencki's equation, $3(C_6H_5.OH) + CH_2O_3 = C_{19}H_{16}O_3 + 2H_2O$ (see *J. pr. Chem.*, **25**, 278), according to which formic acid plays the chief part in the formation of aurin. We now endeavoured to solve the question, Does nascent carbon dioxide really act on phenol so as to yield aurin? To do this we sought to determine the formation of the carbon dioxide under the same conditions as it must be formed in the aurin process, if formed at all. Two test-tubes were taken, and into one of them 2 grams of pure malonic acid and 5 grams of phenol were introduced and well mixed together, and then 10 grams of pure sulphuric acid; into the other the same quantity of malonic acid and sulphuric acid, without any addition of phenol. Both tubes with their contents were now heated at 110° to 120°, when the disengagement of carbonic acid began in both at about the same time and ended after about three hours. In both test-tubes, the whole contents had gone into solution in the sulphuric acid, which was thus merely coloured light brown. After saturation with soda, the two solutions showed as little indication, as regards any coloration produced, of the presence of aurin in the one tube as in the other—in short, not a trace of aurin was formed by the joint action of malonic and sulphuric acids on phenol. Of course in malonic acid $(CO.OH).CH_2.(CO.OH)$, under the circumstances named, the formation of carbonic acid is secured, to the exclusion of that of formic acid.

Compounds of Oxalic Acid with α- and β-Naphthol.

Experiments with the isomeric naphthols showed that these form compounds with oxalic acid similar to that which is formed by phenol.

The *β-naphthol compound* (*β-naphthyl ortho-oxalate*), $\begin{matrix} C_{10}H_7\overset{\beta}{O}.C(OH)_2 \\ | \\ C_{10}H_7\overset{\beta}{O}.C(OH)_2 \end{matrix}$, was obtained by mixing in the right proportions a warm glacial acetic acid solution of β-naphthol and oxalic acid, and heating the mixture with reversed condenser for some hours at the boiling point. It is best to employ a small excess of naphthol, which is subsequently removed with ease on washing the resulting compound with petroleum spirit. The presence of free oxalic acid in the product is thus entirely prevented. On cooling and standing for some time, the compound separates as a crystalline powder, which, after draining off the acetic acid, and drying over lime and calcium chloride, was boiled with

petroleum spirit to remove free naphthol. The substance was then recrystallised from pure glacial acetic acid, and dried in the exsiccator as before. The final product is a perfectly white crystalline powder, melting with slight decomposition at 167°. (Perfectly anhydrous oxalic acid melts with decomposition, as we observed, between 186° and 187°, using capillary tubes in the melting point determination. The melting point of this acid is thus considerably higher than is generally stated in the text-books.)

Analysis gave the following numbers:—

(1.) 0·2748 gram of substance gave 0·7068 gram CO_2.
and 0·1186 „ H_2O.
(2.) 0·2749 „ „ gave 0·7101 „ CO_2.
and 0·1212 „ H_2O.

	Found. (1.)	Found. (2.)	Calculated for $C_{22}H_{18}O_6$.
C =	70·11	70·44 per cent.	69·84 per cent.
H =	4·79	4·90 „	4·76 „

On distillation under the ordinary atmospheric pressure, it is, like the phenol compound, partially decomposed, and the presence of formic acid could be readily detected in the products of distillation by its pungent odour, and the mirror-like metallic reduction of silver from an ammoniacal silver solution. The residue in the retort consisted chiefly of β-naphthol.

This compound is also formed, as well as the α-naphthol compound, by heating oxalic acid and naphthol together at from 120—130° for several hours. When however it is prepared in this way, it is difficult to separate the compound from free oxalic acid. So far as the other properties are concerned, the substance behaves like the phenyl ortho-oxalate.

α-Naphthyl ortho-oxalate, $\begin{matrix} {}^{\alpha}C_{10}H_7O.C(OH)_2 \\ {}^{\alpha}C_{10}H_7O.C(OH)_2 \end{matrix}$.—This compound was prepared in a manner similar to that employed for the β-naphthol-compound. It is, however, not so easily formed as the β-naphthol compound.

The melting point of the substance is 163°, slight decomposition ensuing at that temperature. Its properties and appearance closely resemble those of the β-naphthol compound.

A combustion yielded the following analytical numbers:—

0·2327 gram of substance yielded 0·5929 gram of CO_2,
and 0·1016 „ H_2O.

	Found.	Calculated for $C_{22}H_{18}O_6$.
C =	69·50 per cent.	69·84 per cent.
H =	4·86 „	4·76 „

XLIII.—*On the Composition of the Ash of Wheat-Grain, and Wheat-Straw, grown at Rothamsted, in different Seasons, and by different Manures.*

By Sir J. B. Lawes, Bart., LL.D., F.R.S., F.C.S., and J. H. Gilbert, Ph.D., LL.D., F.R.S., V.P.C.S.

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In the *Journal of the Chemical Society* for 1857, we published a paper entitled:—"On some Points in the Composition of Wheat-Grain, its Products in the Mill, and Bread." In that paper the results of 23 wheat-grain ash-analyses were embodied. The present paper relates to the analyses of 92 wheat-grain and 92 wheat-straw ashes, and including 69 duplicates, the number of complete ash-analyses involved is 253. Every ash is of produce of known history of growth, as to soil, season, and manuring. Thus, there is a series for 16 consecutive seasons, under three very characteristically different conditions as to manuring. There is a series representing nine different conditions as to manuring, each in two unfavourable, and in two favourable seasons for the crop. Lastly, there is a series representing the proportionally mixed produce for the 10 years, 1852–1861, and again for the succeeding 10 years, 1862–1871, for 10 differently manured plots in each case.

The results are thus calculated to illustrate the influence of fluctuations of season from year to year under known, but very different conditions as to manuring; the influence of characteristic seasons under a great variety of manuring conditions; and the influence of continuous supply or exhaustion of certain constituents.

Most of the results have long been waiting for an opportunity of full discussion; but as such opportunity seems still remote, it is proposed now to submit them, arranged in such form as will be convenient for reference; and to accompany the record with only so much of explanation and discussion, as will suffice to indicate the most important conclusions, and usefully to direct the further study of the results.

In explanation of the history of the specimens from which the ashes have been obtained, it should be stated that they have all been grown in the experimental field at Rothamsted, which has now yielded wheat for 40 years in succession, 1844 to 1883 inclusive, respectively without manure, with farmyard manure, and with a great variety of artificial manures; the same manure being, as a rule, applied year after year, to the same plot. The descriptions of wheat grown have been as follows:—1844–1848, Old Red Lammas; 1849–1852, Red Cluster; 1853–1881, Red Rostock; 1882 and since, Club Wheat (red); all of which are well acclimatised, and, with the exception of the first, not very dissimilar varieties.

In the body of the paper, the results of each of the three series of analyses are arranged in Summary Tables, in convenient forms for illustration, and they are given more fully and in more systematic form in the Appendix-Tables I—XV (p. 382, *et seq.*), as under:—

1. The analytical results, excluding sand and charcoal, calculated to 100.*
2. Each constituent calculated per 1000 dry matter of produce.
3. Each constituent calculated per acre, actual produce.

The method of preparing the ashes is as follows:—The substance, generally 20 ounces = 567 grams of wheat-grain, and 12·5 ounces = 354 grams of wheat-straw, is burnt on platinum sheets turned up at the sides and at the back, thus forming dishes about 12 inches long and 4½ inches wide. These are heated in cast-iron muffles, 18 inches long, 3½ inches high, and 5 inches wide at the bottom. Each muffle, which has a flange at the fore part, fits exactly into an orifice in a cast-iron furnace front; and a cast-iron pipe of 1½ inch bore is fixed into the back of the muffle, and passes through the cast-iron furnace back. The muffle rests on a fire brick, so that the fuel is in direct contact only with its sides and top, chiefly the latter, thus lessening bottom heat and, as far as possible, preventing fusion. By this arrangement, the access of dust from the fire is entirely avoided; the ash is burnt by surface, not by bottom heat; the access of air is free, and the incineration is accomplished at a low temperature. Of the 253 ash analyses, nine have been made by Mr. F. A. Manning, and six by Mr. R. Warington. The whole of the remainder (238) have been executed by Mr. R. Richter; the earlier ones in the Rothamsted Laboratory, and the later in his own laboratory at Charlottenburg (Berlin). Mr. Richter has in fact executed about 700 complete analyses of the ashes of various products, animal and vegetable, of known history, prepared at Rothamsted. He

* Where duplicate analyses have been made the mean results are adopted.

has also conducted numerous investigations of method, with the view to testing the limits of accuracy of previous work, and to attain greater accuracy in future; and in the course of these inquiries he has analysed mixtures of precipitates obtained in precisely the same way in series of analyses, to determine their degree of purity, and so on. It is not intended on the present occasion to go into these matters of detail, which of themselves would supply sufficient material for an independent paper.* It will be seen that Mr. Richter's experience has thus been very great; and independently of the confidence in the results which our knowledge of his competency and conscientiousness inspires, their consistency with the history of the specimens, which will be amply illustrated further on, can leave no doubt of their trustworthiness and value. On this point it should be stated in justice to Mr. Richter that all the ashes, duplicates included, have been supplied to him under consecutive numbers, without any indication as to the history of the specimens.

First Series of Analyses.

In our former paper, above referred to, analyses of the grain-ash only, from the produce of eight of the differently manured plots in the first season 1844, of seven in 1845, and of six in 1846, were given; and in two cases duplicate analyses were made, making in all 23. At that time, the plan of applying the same manure to the same plot each year had not been fully adopted; nor were the straw-ashes of those early years analysed. The series now to be considered includes the analyses of both grain-ash and straw-ash, from three of the differently manured plots, in each of 16 consecutive seasons, commencing with the fifth, 1848, and ending with the twentieth, 1863. Two of the three plots have, respectively, been under the same treatment from the first year,

* It may here be remarked, however, that the first and second series of analyses were made more than 15 years ago, since which time there has been much discussion of the details of the magnesium method for the determination of phosphoric acid, by which process nearly the whole of those results were obtained. It is now generally admitted that the conditions of experiment then recommended by the highest authorities are liable to give high results; and Mr. Richter's subsequent investigations of method referred to above, lead him to the same conclusion. The actual results obtained are, however, in all cases adopted; nor would any of the conclusions drawn be affected, if correction had been made in accordance with the indications of the subsequent examinations of method. It should be further stated that indications of the presence of manganese in probably determinable quantity having been observed in some wheat grain-ashes, some quantitative estimations were made, and the amounts found corresponded to a mean of 0·26 per cent. Mn_3O_2. The indications in the case of straw-ashes have not been such as to lead to quantitative determinations being made; but it may be supposed that the amount of manganese in them would at any rate not be less than in the grain-ashes.

1844, and the third has been substantially so from the second year, 1845, as explained more in detail below.

The three plots are:—

Plot 2. Farmyard manure, 14 tons per acre, every year from the commencement.

Plot 3. Unmanured, every year from the commencement.

Plot 10*a*. First year (1844), a mineral manure consisting of superphosphate of lime, and a crude silicate of potash; second year, 168 lbs. sulphate, and 168 lbs. muriate of ammonia of commerce, per acre; third year, 224 lbs. sulphate of ammonia; fourth and fifth years, 150 lbs. sulphate and 150 lbs. muriate; sixth and each succeeding year, 200 lbs. sulphate and 200 lbs. muriate of ammonia, per acre per annum.

The conditions of growth, so far as the supply of constituents by manure is concerned, were therefore very widely different in the three cases. Thus, the produce of Plot 2, with farmyard manure, was grown under the influence of an excessive supply both of nitrogen and of mineral, or ash-constituents; that of Plot 3, unmanured, under conditions of exhaustion of both nitrogen and ash-constituents; and that of Plot 10*a* (receiving ammonium-salts alone), with an excess of supplied nitrogen, but with great relative deficiency of ash-constituents. If, therefore, the composition of the ash of the produce is directly affected by the available supply of ash-constituents within the soil, we should expect very marked differences in the composition of the ash in the three cases.

The Appendix-Tables I, II, and III (pp. 382–387), give the percentage composition of the pure grain-ash, and the pure straw-ash, for each of the 16 consecutive years: I, for the farmyard manure plot; II, for the unmanured plot; and III, for the plot with ammonium-salts alone. By the term "pure" ash is meant the ash excluding sand and charcoal. Referring to these Appendix-Tables for the full details, the results will be discussed chiefly by the aid of a series of summary tables.

The following summary Table, I, brings prominently to view some important facts, and indicates some important conclusions. There is there given for each of the three differently manured plots, the highest, the lowest, and the mean percentages of potash and phosphoric acid, in the grain-ash, and in the straw-ash, in the 16 consecutive years. There is thus shown the extreme range of variation in the composition of the ash in some important particulars, with the same manure in very various seasons, and also the range with the different manures. It may be observed that the two constituents selected for illustration together contribute between 80 and 85 per cent. of wheat grain-ash.

TABLE I.

Highest, Lowest, and Mean Percentages of Potash and Phosphoric Acid *in the Pure Ash*, in 16 Consecutive Seasons.

Plots.	Manures.	Per cent. in grain-ash.			Per cent. in straw-ash.		
		Highest.	Lowest.	Mean 16 years.	Highest.	Lowest.	Mean 16 years.
		Potash.					
2	Farmyard manure	35·5	27·2	31·6	25·6	12·9	18·3
3	Unmanured	35·5	29·7	33·0	20·7	10·5	14·6
10*a*	Ammonium-salts alone	35·9	28·1	33·4	23·4	10·5	16·5
		Phosphoric Acid.					
2	Farmyard manure	54·7	47·1	51·7	6·21	2·98	3·79
3	Unmanured	52·6	45·6	49·7	5·96	2·98	3·79
10*a*	Ammonium-salts alone	52·9	43·4	47·3	4·34	1·73	3·09

A glance at the table shows that in both grain-ash and straw-ash there is, in the case of both constituents, a much wider range of variation in their percentage in the ash with the same manure in different seasons, than there is in the mean percentage under each of the three very characteristically different conditions as to manuring.

Thus, the percentages of potash in the grain-ashes in the 16 seasons range—with farmyard manure, from 35·5 to 27·2; without manure, from 35·5 to 29·7; and with ammonium-salts alone, from 35·9 to 28·1. But the mean percentage over the 16 years only ranges between 31·6 with farmyard manure, 33·0 without manure, and 33·4 with ammonium-salts alone. The amount of potash in the straw-ashes shows a still greater range in different seasons with the same manure, and comparatively small differences in the mean percentages under the influence of the different manures. Thus, the variation in the percentage of potash in the straw-ashes according to season is—with farmyard manure, from 25·6 to 12·9; without manure, from 20·7 to 10·5; and with ammonium-salts alone, from 23·4 to 10·5; whereas the difference between the mean percentages over the 16 years is, under the three different conditions as to manuring, very much less, the mean amounts being with farmyard manure 18·3, without manure 14·6, and with the ammonium-salts 16·5.

The facts relating to phosphoric acid are equally striking. Thus, its percentage in the grain-ash ranges, according to season—with farmyard manure, from 54·7 to 47·1; without manure, from 52·6 to 45·6; and with ammonium-salts, from 52·9 to 43·4; but the difference between the mean percentages under each condition of manuring over the 16 years, is only as follows:—with farmyard manure 51·7, without manure 49·7, and with ammonium-salts 47·3. Again, the variation in the percentage of phosphoric acid in the straw-ashes is, according to season—with farmyard manure, from 6·21 to 2·98; without manure, from 5·96 to 2·98; and with ammonium-salts alone, from 4·34 to 1·73; whereas the mean percentage over the 16 years is—with farmyard manure 3·79, without manure 3·79, or exactly the same as with farmyard manure, and with ammonium-salts alone 3·09.

With both potash and phosphoric acid, therefore, there is very great difference in the percentage in the ash of both grain and straw, according to season, and very much less difference in the mean percentage according to manure. With few exceptions, a similar result is observed with other constituents.

What is the significance of these facts? In the first place it is that the character of development of a crop left to ripen, depends very much more upon season than upon manuring. Indeed, if one crop (of wheat for example) grows side by side with another of exactly the same description, but yielding under the influence of manure twice the amount of produce, and both under such conditions of season that each fully and normally ripens, the composition of the final product, the seed, will be very nearly identical in the two cases. In other words, there is scarcely any difference in the composition of the truly and normally ripened seed. But, as variations of season affect the character of development, and the conditions of maturation, there may obviously be, with these, very wide differences in the composition of the product. The wide range in the composition of the ash of the grain, which the table shows according to season, represents in fact a corresponding deviation from the normal development.

It should be noted that the highest and the lowest percentages of both potash and phosphoric acid in the grain-ashes, as given in the tables, are in the produce of very unfavourable seasons, thus further showing how varied are the characters of development dependent on the varying external conditions of season. In the case of the straw ashes, the highest percentages of potash are not, but the lowest are, in the produce of unfavourable seasons; and the highest percentages of phosphoric acid are, and the lowest are not, in unfavourable seasons. The differences between the grain-ashes and the straw-ashes in these respects will be better understood as we proceed. But it may be remarked in passing that the results are connected with the

facts that unfavourable seed-forming and ripening conditions may supervene on conditions of high or of low luxuriance, that is, of great or limited activity of accumulation of constituents by the plant; or, on the other hand, favourable seed-forming and ripening conditions may supervene on very various conditions as to previous accumulation.

Table II shows the variation according to season and manure, not in the percentage composition of the ash, but in the amount of potash and phosphoric acid *per* 1000 *dry substance* of the grain and the straw respectively. This mode of representation obviously brings more prominently to view the variations in the proportion of the two ash-constituents to the organic substance produced.

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TABLE II.

Highest, Lowest, and Mean Amounts of Potash and Phosphoric Acid *per* 1000 *Dry Substance.*

Plots.	Manures.	Per 1000 dry grain.			Per 1000 dry straw.		
		Highest.	Lowest.	Mean 16 years.	Highest.	Lowest.	Mean 16 years.
				Potash.			
2	Farmyard manure	7·79	5·38	6·35	18·37	9·06	11·91
3	Unmanured	8·38	6·01	6·62	14·16	6·96	9·30
10*a*	Ammonium-salts alone	7·38	5·15	6·02	13·24	5 69	8·71
				Phosphoric Acid.			
2	Farmyard manure	11·10	9·65	10·44	4·12	1·49	2·45
3	Unmanured	10·75	8·98	10·03	3·74	1·65	2·42
10*a*	Ammonium-salts alone	10·03	7·18	8·54	3·47	0·93	1·63

It is here seen that the proportion of both potash and phosphoric acid to the organic substance, even of the grain, which, if normally ripened, is assumed to be a comparatively uniform product, varies very considerably according to season; whilst, at any rate as between the grain grown by farmyard manure, and that grown without manure, the mean proportion over the 16 years differs but little. The grain grown under the influence of the ammonium-salts alone, that is, as will afterwards be further illustrated, under conditions of

very abnormal mineral exhaustion, shows not only a wide range in the proportions of both potash and phosphoric acid, especially the latter, according to season, but much lower mean amounts than either with farmyard manure or without manure. In the straw, the range of variation is seen to be much wider still according to season; and it is considerable also according to manure. In the case of straw, we should not expect the amounts of mineral constituents finally retained to bear so uniform a proportion to the organic substances as in that of the grain. Besides the amounts of mineral constituents that may be essential to the organic formations of the straw itself, there will be a variable quantity accumulated in the plant, and not finally appropriated by the seed.

The next point to consider is—what is the connection between high or low amount of the different ash-constituents and the quality of the produce? Table III (pp. 314–315) is arranged to illustrate this. The question here arises, what is the proper measure of quality of produce? So far as the grain is concerned, the weight per bushel, although by no means a perfect measure, is at any rate the best single character recognised in practice. High and equal weight, or low and equal weight, may, however, respectively be accompanied by different characters in other respects. But grain of high weight per bushel would be classed by the farmer and miller as of good, and grain of low weight, of bad quality. It is to be regretted that the average weight of a given number of seeds, or the number of seeds contributing to a given weight, has not been determined; but, in defect of such data, we adopt weight per bushel as the best conventional measure of quality at our command.

The produce of the 16 years on each of the three plots is arranged in the Table (III), in the order of highest weight per bushel; and other characters which have also to be taken into account, are given side by side. Thus, in the succeeding columns of the table are given, the quantity of grain to 100 straw, the quantity of produce (grain, straw, and total) per acre in lbs.; and the percentages of pure ash and of nitrogen in the dry matter of the grain. Lastly, in the columns to the right of those showing these general characters, are recorded the percentages of some selected constituents in the grain-ash (pure), and the proportion of the same constituents in 1000 dry substance of the grain. The upper division of the Table gives the results for the produce of the farmyard manure plot, the middle division for the unmanured plot, and the lower division for the plot with ammonium-salts alone.

The Table (III), shows that, under each of the three conditions as to manuring, the eight seasons of higher weight per bushel also yield on the average a higher proportion of grain to straw,

and higher amounts of produce, than the eight of lower weight per bushel. But although there is with high average weight per bushel of the grain, this general tendency to higher characters of produce in other respects, the coincidence of these characters is very far from being borne out in detail.

Thus, with farmyard manure, the season giving the highest weight per bushel (1849) gives considerably less than the average amount per acre of both grain and straw, especially the latter, and although high, not the highest proportion of grain to straw. Again, of the three years of highest amount of total produce, 1863, 1854, and 1859, the two former give high weight per bushel of grain, but 1859 a very low weight per bushel. The fact is, as already alluded to, high character of grain, as indicated by high weight per bushel, which depends on favourable ripening and harvest weather, may supervene on conditions either of restricted growth, or of high luxuriance—that is, high vegetative activity and great accumulation.

Without manure, the year of highest weight per bushel (1863) is one of about average amount of produce on that plot, and of high, but not the highest proportion of grain to straw.

With ammonium-salts alone, the year of highest weight per bushel (1863) is also the year of highest total produce, and of nearly the highest proportion of grain to straw with that manure.

Again, with each condition as to manuring, there is with high quality of grain, as shown by high weight per bushel, a general and marked, but not uniform tendency to low percentage of total mineral constituents (ash), and also low percentage of nitrogen, in the dry substance of the grain. That is to say, the higher quality of the grain is connected with a greater accumulation of the non-nitrogenous matters primarily derived from the atmosphere, in proportion to the amounts of the soil-derived ash-constituents and the nitrogen, which have been stored up. In fact, in comparable cases, high quality of grain means high proportion of carbohydrates (starch), and coincidently low proportion of nitrogenous substances.

As there is lower percentage of total ash with higher quality of grain, there is necessarily a lower proportion of individual mineral constituents in the dry substance. Accordingly, with each of the three conditions as to manuring there is—taking the average of the eight years of highest weight per bushel—almost without exception a lower proportion of each of the individual mineral constituents in the dry substance of the grain than on the average of the eight years of lower weight per bushel. This is more or less the case with lime, magnesia, potash (soda), phosphoric acid (sulphuric acid), and silica. The actual amount of silica is in all cases small; but the difference in the amount is greater than that of any of the

Table III.

General Characters of the Produce; *percentage* of Selected Constituents *in the* *of Grain.* Harvests in order of

	Harvests.	Weight per bushel, lbs.	Grain to 100 straw.	Produce, per acre, lbs.			Per cent. in dry matter.		Per cent. in grain ash (pure).		
				Grain.	Straw.	Total.	Nitrogen.	Ash (pure).	Lime.	Magnesia.	Potash.
Plot 2.—Farmyard Manure.	1849.....	63·8	68·3	2068	3029	5097	1·58	1·93	2·52	10·6	33·1
	1851.....	63·6	66·2	2049	3094	5143	1·57	1·93	2·88	11·1	32·4
	1863.....	63·1	67·5	2886	4279	7165	1·52	1·85	2·34	11·4	31·5
	1858.....	62·6	65·5	2512	3837	6349	1·91	2·04	2·61	11·2	31·9
	1854.....	62·5	60·1	2675	4450	7125	1·70	1·98	2·46	11·3	32·0
	1855.....	62·0	58·2	2237	3845	6082	2·19	2·08	2·49	11·0	30·9
	1850.....	61·9	57·3	1861	3245	5106	1·86	2·04	2·80	11·1	31·4
	1862.....	61·0	58·3	2447	4195	6642	1·57	1·99	2·51	11·1	32·0
	Mean ...	62·6	62·5	2342	3747	6089	1·73	1·98	2·58	11·1	31·9
	1861.....	60·5	71·0	2202	3101	5303	1·95	2·15	2·52	10·3	33·1
	1857.....	60·4	77·9	2587	3323	5910	1·97	1·94	2·88	12·0	29·8
	1856.....	58·6	52·8	2277	4317	6594	1·89	1·98	2·53	11·7	29·3
	1848.....	58·2	56·0	1705	3041	4746	1·89	2·03	2·41	10·8	30·2
	1852.....	58·2	49·6	1716	3457	5173	2·02	1·98	2·79	12·8	27·2
	1859.....	56·5	47·1	2263	4810	7073	2·09	2·11	2·37	11·2	31·2
	1860.....	55·5	54·2	1864	3440	5304	2·00	2·15	2·78	10·1	33·8
	1853.....	51·1	33·2	1120	3372	4492	1·76	2·20	2·60	10·2	35·5
	Mean ...	57·4	54·5	1967	3607	5574	1·96	2·06	2·61	11·1	31·3
Plot 3.—Unmanured.	1863.....	62·7	70·4	1127	1600	2727	1·65	1·95	2·66	10·9	32·3
	1849.....	61·4	76·1	1229	1614	2843	1·73	1·88	3·15	9·7	35·2
	1851.....	61·1	66·6	1083	1627	2710	1·67	1·94	2·98	10·2	34·7
	1854.....	60·6	63·6	1359	2137	3496	1·92	1·95	2·67	10·4	34·2
	1850.....	60·6	58·2	1002	1719	2721	1·83	2·02	2·98	9·9	33·0
	1858.....	60·4	68·3	1141	1670	2811	1·86	2·02	2·76	10·5	32·7
	1855.....	59·2	60·0	1072	1787	2859	2·14	2·02	2·64	9·9	33·9
	1857.....	58·3	78·3	1236	1577	2813	1·91	1·92	3·39	10·8	32·0
	Mean ...	60·5	67·4	1156	1716	2872	1·84	1·96	2·90	10·3	33·5
	1862.....	57·8	58·2	996	1713	2709	1·76	2·03	2·54	10·2	32·3
	1861.....	57·4	58·7	736	1254	1990	2·04	2·19	2·68	9·6	34·4
	1848.....	57·3	55·6	952	1712	2664	2·17	2·00	2·87	10·4	31·2
	1852.....	56·6	53·9	860	1597	2457	2·08	2·03	2·87	11·7	29·7
	1856.....	54·3	57·3	892	1558	2450	1·91	2·04	2·55	10·8	30·6
	1860.....	52·6	50·6	738	1459	2197	1·92	2·16	2·71	9·1	33·6
	1859.....	52·5	48·3	1051	2175	3226	1·96	2·08	2·75	11·0	31·9
	1853.....	45·9	25·4	359	1413	1772	2·09	2·36	3·09	10·3	35·5
	Mean ...	54·3	51·1	823	1610	2433	1·98	2·08	2·76	10·4	32·4
Plot 10A.—Ammonium-salts alone.	1863.....	62·6	74·3	2587	3481	6068	1·70	1·56	3·85	11·2	34·4
	1849.....	62·3	75·1	2141	2851	4992	1·95	1·67	3·46	10·3	35·6
	1851.....	61·9	64·0	1966	3070	5036	2·15	1·81	3·51	10·7	32·6
	1854.....	60·5	61·5	2211	3597	5808	2·30	1·72	3·36	10·2	35·8
	1850.....	60·2	55·7	1721	3089	4810	2·13	1·86	3·63	10·7	33·2
	1858.....	59·6	67·6	1439	2130	3569	2·23	1·90	4·05	10·5	33·5
	1848	58·1	56·3	1334	2367	3701	2·42	1·95	3·22	10·8	30·6
	1857.....	58·0	75·9	1816	2392	4208	2·08	1·63	4·38	11·7	31·6
	Mean ...	60·4	66·2	1902	2872	4774	2·09	1·74	3·68	10·8	33·4
	1855.....	57·1	51·2	1285	2512	3797	2·40	1·91	3·57	10·4	34·7
	1862.....	56·5	56·2	1457	2593	4050	1·89	1·84	3·54	10·7	34·2
	1852.....	55·9	47·3	1320	2787	4107	2·48	1·83	3·51	12·7	28·1
	1856.....	55·6	53·4	1505	2818	4323	2·23	1·85	3·61	11·4	31·9
	1861.....	55·0	44·2	854	1930	2784	2·08	2·00	3·47	10·0	35·5
	1859.....	51·5	44·2	1207	2730	3937	2·30	1·86	3·64	11·2	32·7
	1860.....	49·5	40·9	905	2213	3118	2·24	2·12	3·41	9·1	34·8
	1853.....	48·6	31·3	642	2049	2691	2·43	1·98	3·75	9·3	35·9
	Mean ...	53·7	46·7	1147	2454	3601	2·25	1·91	3·56	10·6	33·5

Table III.

Grain-Ash (pure), and amount of the Ash-Constituents *per* 1000 *Dry Matter* Highest Weight per bushel of Grain.

Per cent. in grain ash (pure).			Per 1000 of dry matter of grain.						Harvests.
Phosphoric acid.	Sulphuric acid.	Silica.	Lime.	Magnesia.	Potash.	Phosphoric acid.	Sulphuric acid.	Silica.	
50·3	1·51	0·53	0·49	2·03	6·37	9·7	0·29	0·10	1849
50·7	0·92	0·66	0·55	2·15	6·25	9·8	0·18	0·13	1851
52·0	0·93	0·65	0·43	2·12	5·85	9·7	0·17	0·12	1863
51·9	0·75	0·49	0·53	2·28	6·52	10·6	0·15	0·10	1858
52·2	0·47	0·50	0·49	2·24	6·34	10·4	0·09	0·10	1854
53·3	0·03	0·70	0·52	2·29	6·43	11·1	0·01	0·14	1855
50·5	1·42	0·92	0·57	2·27	6·41	10·3	0·29	0·19	1850
51·6	0·51	0·83	0·50	2·22	6·37	10·3	0·10	0·16	1862
51·6	0·83	0·66	0·51	2·20	6·30	10·2	0·16	0·13	Mean
51·4	1·01	0·50	0·54	2·21	7·12	11·1	0·22	0·11	1861
52·5	0·46	0·49	0·56	2·32	5·79	10·2	0·09	0·10	1857
54·2	0·23	0·75	0·50	2·32	5·80	10·7	0·05	0·15	1856
52·7	0·55	1·56	0·49	2·19	6·11	10·7	0·11	0·32	1848
54·7	0·14	0·99	0·55	2·53	5·38	10·8	0·03	0·20	1852
52·6	0·51	0·80	0·50	2·36	6·58	11·1	0·11	0·17	1859
49·4	0·87	1·28	0·60	2·18	7·27	10·7	0·19	0·27	1860
47·1	2·35	0·93	0·57	2·23	7·79	10·3	0·52	0·20	1853
51·8	0·76	0·91	0·54	2·29	6·40	10·7	0·14	0·18	Mean
51·6	0·67	0·59	0·52	2·12	6·28	10·0	0·13	0·12	1863
47·7	1·83	0·74	0·59	1·83	6·65	9·0	0·34	0·14	1849
49·1	1·13	0·72	0·58	1·97	6·75	9·5	0·22	0·14	1851
49·4	1·56	0·45	0·52	2·04	6·67	9·6	0·31	0·09	1854
49·7	1·14	1·11	0·60	1·99	6·65	10·0	0·23	0·23	1850
50·9	0·66	0·97	0·56	2·12	6·61	10·3	0·13	0·20	1858
50·8	0·65	0·92	0·53	2·01	6·86	10·3	0·13	0·19	1855
50·0	1·28	0·97	0·65	2·08	6·16	9·6	0·25	0·19	1857
49·9	1·12	0·81	0·57	2·02	6·56	9·8	0·23	0·15	Mean
49·6	1·60	1·18	0·51	2·08	6·56	10·1	0·33	0·24	1862
47·5	1·66	2·51	0·59	2·09	7·54	10·4	0·36	0·55	1861
51·4	0·79	1·34	0·57	2·07	6·25	10·3	0·16	0·27	1848
51·8	0·99	1·31	0·58	2·36	6·01	10·5	0·20	0·27	1852
52·6	1·06	1·00	0·52	2·19	6·23	10·7	0·22	0·20	1856
47·4	2·21	2·37	0·59	1·98	7·26	10·3	0·48	0·51	1860
50·6	1·25	1·06	0·57	2·28	6·64	10·5	0·26	0·22	1859
45·6	2·40	1·25	0·73	2·43	8·38	10·8	0·57	0·30	1853
49·6	1·50	1·50	0·58	2·17	6·70	10·4	0·29	0·30	Mean
46·0	2·37	0·86	0·60	1·75	5·37	7·2	0·37	0·13	1863
45·9	2·70	0·86	0·58	1·72	5·93	7·7	0·45	0·14	1849
49·6	1·46	0·64	0·64	1·93	5·89	9·0	0·26	0·11	1851
46·1	2·23	0·72	0·58	1·74	6·15	7·9	0·38	0·12	1854
49·2	1·54	0·60	0·68	1·99	6·18	9·2	0·29	0·11	1850
46·7	2·78	1·01	0·77	1·99	6·35	8·9	0·53	0·19	1858
51·3	0·78	1·42	0·63	2·11	5·98	10·0	0·15	0·28	1848
47·0	2·12	1·51	0·72	1·90	5·16	7·7	0·34	0·25	1857
47·7	2·00	0·95	0·64	1·87	5·84	8·3	0·36	0·16	Mean
47·5	1·58	0·97	0·68	1·97	6·61	9·1	0·30	0·18	1855
44·3	2·91	1·80	0·65	1·98	6·30	8·2	0·54	0·33	1862
52·9	0·61	1·04	0·64	2·33	5·15	9·7	0·11	0·19	1852
50·1	1·00	1·11	0·67	2·11	5·88	9·3	0·19	0·20	1856
44·6	2·63	1·68	0·69	2·00	7·12	8·9	0·53	0·34	1861
47·2	2·36	1·17	0·68	2·09	6·09	8·8	0·44	0·22	1859
43·4	3·57	2·60	0·72	1·94	7·38	9·2	0·76	0·55	1860
44·7	2·45	1·82	0·74	1·85	7·09	8·8	0·49	0·36	1853
46·8	2·14	1·52	0·68	2·05	6·32	9·0	0·39	0·28	Mean

other constituents; being, without manure, and with ammonium-salts alone, nearly twice as high on the average of the eight years of low quality of grain as over the eight of higher quality. It is, moreover, remarkable that the grain grown by farmyard manure, which supplies a large amount of available silica, shows a smaller proportion of it in its dry substance than that grown either without manure or by ammonium-salts alone.

It may here be observed that the higher proportion of silica in the dry substance with lower conditions of maturation of the produce, is very marked in the case of the straw also. Thus, with farmyard manure, the average proportion of silica per 1000 dry substance of the straw is 41·7 over the eight years of highest maturation, and over the eight of lowest maturation 44·6; without manure, with the years of best ripening, it is 42·7, and with those of the worst ripening 47·5; and with the ammonium-salts alone it is 32·1 over the eight best, and 37·3 over the eight worst seasons.

This result is quite inconsistent with the usually accepted view that high quality and stiffness of straw depend on high amount of silica. Pierre and Bretschneider have, however, concluded from their experiments that this is not the case, and we have ourselves long maintained a contrary view. In fact, high proportion of silica means relatively low proportion of organic substance produced. Nor can there be any doubt that strength of straw depends on favourable development of the woody substance; and the more this obtains the more will the accumulated silica be, so to speak, diluted—in other words, show a lower proportion to the organic substance. Further evidence will be adduced on this point as we proceed. It may be mentioned, however, that in this neighbourhood, where the straw-plait industry prevails, the complaint during the last few seasons of bad harvests has been that an unusually large proportion of the straw is brittle and breaks in the working; and considering the character of the seasons there can be no doubt that this is associated with low development of the woody matter and high proportion of silica.

It will be well to go a little more into detail in reference to other individual mineral constituents; and first as to the proportion of potash in the dry substance of the grain in the different seasons.

With each condition as to manuring, there is not only a lower average proportion of potash, but a much greater uniformity in the proportion, in the eight seasons of higher, than in the eight of lower quality of grain. The chief exceptions to uniformity in the eight years of higher quality are, with farmyard manure in 1863, without manure in 1863 and 1857, and with ammonium-salts again in 1863 and 1857. In these years the proportion of potash was, though not

actually the lowest in the 16 years, considerably below the average. The season of 1863, which shows a low proportion of potash under each of the three conditions as to manuring, was not only the one of the greatest luxuriance, as shown by the yield of total produce (grain and straw), but it was the one of highest produce of grain throughout the 40 years of the experiments 1844 to 1883 inclusive, both in the experimental field and in the country at large. The other season of low proportion of potash in the grain, 1857, was one of lower than average growth of straw; but, owing to high summer temperature and less than the average fall of rain, the season was very favourable for seed-formation; but with some excess of rain about harvest time the weight per bushel was low. Both these seasons of low proportion of potash were therefore seasons of high grain productiveness, and the low proportion of potash is due, not to deficiency of potash, but to high accumulation of organic substance. In fact in 1863, the quantity of potash per acre in the total crop, under each condition of manuring, was more than over the average of seasons; and in 1857 the quantity per acre in the grain was more than in the grain on the average of seasons.

Very different, however, were the conditions of season, and of crop, under which absolutely the lowest proportion of potash in the grain throughout the 16 years was found. With each condition as to manuring, the actually lowest proportion of potash in the dry substance of the grain was in 1852, which yielded less than the average amount of both grain and straw, lower than average proportion of grain to straw, and grain of very low weight per bushel. The spring had been dry, cold, and backward, the early summer rainy and cold, and the seed-forming and maturing period variable, with a good deal of hot weather, but some heavy storms. Here then the low proportion of potash in the grain (and it was very low in the straw also, even on the farmyard manure plot) was due to defective conditions of season, for growth, for seed-formation, and for maturation.

It is remarkable that whilst it is with good seasons that we have a comparatively uniform and low proportion of potash in the dry substance of the grain, it is with a very bad season that we have actually the lowest proportion; and it is again in nearly the worst season of our whole series of 40 years that there is actually the highest proportion of potash in the dry substance. Thus, in 1853 we have, with farmyard manure and without manure, the highest, and with ammonium-salts alone, very high proportion of potash in the grain, with at the same time the lowest amount of produce, the lowest proportion of grain to straw, and the lowest weight per bushel of grain throughout the 16 years. The conditions of growth were that, owing to an extremely wet autumn and winter, the seed could not be sown

until the spring; the spring was unseasonably cold and wet, and the summer colder than the average, and very wet. The high proportion of potash was thus due to defective accumulation of organic substance under the influence of unfavourable climatic conditions.

These details as to the proportion of potash in the dry substance of the grain illustrate in a very striking manner the greater influence of season than of manuring on the mineral composition of the grain. With favourable seasons there is comparatively little variation; but with unfavourable seasons there is very great variation, sometimes much lower, but sometimes much higher, and on the average higher proportions of potash than in favourable seasons. Nor is there evidence that there is, comparing one season with another, high proportion of either lime, magnesia, or soda, with low proportion of potash, or *vice versâ*. Comparing the average results of one plot with those of another, however, there is, with the small produce without manure, even a rather higher proportion of both potash and lime, but lower of magnesia than with farmyard manure. With ammonium-salts alone, on the other hand, where there is great exhaustion of mineral constituents having regard to the amount of crop grown, there is a distinctly lower average proportion of both potash and magnesia, and a rather high proportion of lime. The conclusion is, that with normal maturation there is nearly uniform composition, and that the deviations from normal mineral composition are associated with deviations from normal development of the organic substance.

It will be well to call attention, though more briefly, to the connection between the character of the produce and the proportion of phosphoric acid it contains. As with potash, so also with phosphoric acid, there is with each of the three conditions as to manuring, a lower average proportion in the dry substance of the grain over the eight better, than over the eight worse seasons; and the proportion is generally the lowest in the individual seasons of high quality of grain. There is, however, with lower average and lower individual proportions of phosphoric acid in the better seasons, a wider range of variation than in the seasons of lower quality of grain; and also a wider range of variation than in the case of the potash. In the case of the farmyard manure plot at any rate, it cannot be supposed that the low proportions of phosphoric acid in the dry substance of the grain of the better seasons are due to deficient supply. The indication is indeed, as with the potash, that the low proportion with high quality of grain is the result of enhanced accumulation of organic substance, by which the proportion of the mineral constituents is reduced. On this view, a relatively low proportion of any one constituent may be due to its favourable action, and will by no means necessarily imply either deficient supply, or that it has been without beneficial effect.

Comparing, however, the results for the three different plots with one another, the question of supply or exhaustion obviously comes in. It is seen that the proportion of phosphoric acid in the dry substance of the grain is lower without manure than with farmyard manure, and much lower still with ammonium-salts alone. Other evidence will be given further on, showing that with ammonium-salts alone there was doubtless very abnormal exhaustion of phosphoric acid. Further, there is unmistakeable evidence of increase in the proportion of sulphuric acid with the decrease in that of phosphoric acid, though not in amount to compensate for the deficiency.

The question here arises, how far the phosphoric acid and sulphuric acid found in the ash are due to the oxidation of phosphorus and sulphur in the burning? The evidence at command leads to the conclusion that the existing phosphorus and sulphur are at any rate only in part so oxidated. On the other hand, the evidence goes to show that sulphuric acid is liable to be expelled in the incineration, in presence of acid phosphates, or much silica, or to be reduced by charcoal if there be not sufficiently free access of air. In the method of burning adopted at Rothamsted, there is probably a minimum liability to loss from such reduction. As bearing upon the question of the probability of loss of sulphuric acid (and chlorine) by expulsion in presence of acid phosphates or silica, it may be mentioned that, excluding the ferric oxide on the one hand, and the silica on the other, and calculating the whole of the phosphoric acid as tribasic, the grain-ashes show more than one and a half time as much acid as base; and even calculating the whole of the phosphoric acid, whether combined with alkalis or earths, as only bibasic, there is still an excess of acid. On the other hand, the straw-ashes, calculated in the same way, show a considerable excess of base, even when the whole of the phosphoric acid is reckoned as tribasic; but they contain more than 60 per cent. of silica. The question arises, therefore, whether carbonic acid (from organic acids or carbonates as such), and some sulphuric acid and chlorine, have not been expelled in the burning; in the case of the grain-ashes, in the presence of acid phosphates, and in that of the straw-ashes, in the presence of an excess of silica.

Referring to the control of ash-analyses, Bunsen maintains that by treating the ash with carbonic acid, and subsequent evaporation, all the bases present are converted into neutral salts; and that the results of the analysis can only be considered satisfactory, when the sum of the quotients obtained by dividing the weights of the individual bases by their equivalent weights, is very approximately equal to the sum of the quotients of the amounts of the acids found, divided by their equivalents. In other words, acids and bases must stand in

such relation to one another as to form neutral salts without leaving any residue.

It seems difficult to suppose that the analyses of the ashes of wheat-grain and wheat-straw, such as those recorded in this paper, could be so proved to be correct. Thus, in the case of the grain-ashes, the basicity of the phosphoric acid must be calculated as may be required to give neutral salts; and in the case of the straw-ashes as much of the silica as may be required must be brought in.

Unfortunately we have not complete analyses of the ash of the separate mill-products of wheat-grain, but in our former paper (this Journal, 1857) we gave the amounts of nitrogen, and of total ash, in some series of such products, and the amount of phosphoric acid and magnesia in selected cases. Dempwolf has, however, given most of the constituents in a complete series of mill-products (*Ann. Chem. Pharm.*, 1869, **149**, 343), and so far as the constituents, nitrogen, phosphoric acid, and magnesia, which we also determined, are concerned, his results and our own are generally accordant. Within the range of the white flours, there is very generally a slight increase in the percentage of nitrogen proceeding from the finer to the coarser. There is a more marked increase in the percentage of nitrogen in the more branny products, though it is not quite so high in the purest bran as in the products next above it in the series; the greatest concentration of nitrogenous substances being immediately below the pericarp itself.

Referring to the distribution of the several ash-constituents, it may be stated that, according to the data referred to, the amount of potash and of lime in proportion to a given weight of organic substance increases somewhat more rapidly than does that of the nitrogen, proceeding from the finer to the coarser white flours, that of magnesia does so in a greater degree still, and that of the phosphoric acid in about the same degree as the potash. The proportion of all the constituents mentioned is very much greater in the more branny portions. Thus, the proportion of potash is about 10 times as high in the dry substance of the bran as in that of the finer flours; the proportion of lime is 4 or 5 times as high; that of magnesia 15 to 20 times, and that of phosphoric acid more than 10 times as high. Our own experiments showed about 15 times as much magnesia, and about 10 times as much phosphoric acid in the dry substance of the bran as in that of the white flours. Again, experiments of W. Mayer (*Ann. Chem. Pharm.*, 1857) showed about 14 times as much phosphoric acid in the dry substance of bran as in that of the finest flour.

In fact the more the cereal grain, which is characteristically a starchy product, is perfectly matured, the higher will be the proportion of flour, as a rule the lower will be the proportion of nitrogenous

substances, the lower that of the bran, and the higher that of starch. It is obvious from the facts quoted above, that the more these characters are developed, the lower should be the proportion of the mineral constituents in the total grain; and the results which have been discussed have consistently shown a lower proportion of mineral constituents in the produce of the seasons of favourable maturation.

Table III (pp. 314-315) also shows, as has been referred to, a generally lower percentage of nitrogen in the better matured grains, that is, in those in which more starch has been accumulated. In reference to this point, it may be stated that in 1847 we took samples of a growing wheat crop at different stages of its progress, commencing on June 21, and determined the dry matter, ash, and nitrogen in them. Calculation of the results showed that whilst during little more than five weeks from June 21, there was comparatively little increase in the amount of nitrogen accumulated over a given area, more than half the total carbon of the crop was accumulated during that period. Consistently with this, Professor R. C. Kedsie, and the late Professor R. F. Kedsie have recently shown by a series of experiments in which they partially analysed samples of a wheat crop cut on 21 consecutive days, commencing June 26, 1879, that with increase in the weight of the kernels there was, especially in the earlier stages, a decrease in the percentages of nitrogen, cellulose, and mineral matter; whilst calculated per acre at the different periods, there was an increase in the actual amount of nitrogen stored up over a given area up to a given point, but a considerably greater increase in the quantity of carbohydrates accumulated in the same time over the same area.

Again, in a very comprehensive investigation of the composition of American wheats, conducted by Mr. Clifford Richardson, under the auspices of the Department of Agriculture at Washington, he finds a generally low average percentage of albuminoïds in American as compared with European wheats; and he concludes that this is indication of inferiority of quality, in many cases due to deficient supply of nitrogen by the soil. It is more probably due to enhanced formation of starch under the influence of high ripening temperature. In our former paper, we discussed the point as far as the data then at command permitted, and we concluded that high percentage of total nitrogenous substance was by no means a characteristic of the wheats held in the highest estimation either by the miller or the baker; and that so far as both the baker and the consumer are concerned, the condition of the nitrogenous matters is of more importance than their total amount. Comparing one description of wheat with another, the one with a relatively high percentage of nitrogen may be the better, provided the grain be at the same time fully ripened, and not too horny. But when the percentage exceeds a certain limit, the grain is

generally either too hard, or there is deficient storing up of starch, and an unfavourable condition of the nitrogenous substances. In fact, comparing the grain grown from the same description of seed, but on different soils, or in different seasons, high percentage of total nitrogenous matter is almost invariably coincident with inferior maturation.

The next point to consider is the bearing of the results relating to the three plots, as to the influence of full supply or of exhaustion on the mineral composition of the grain.

Table IV (pp. 324–325) shows the average amounts obtained *per acre*, of grain, straw, and total produce, also of nitrogen, ash, and each mineral constituent in them, over the first eight, the second eight, and the sixteen years, under each of the three conditions as to manuring.

Table V (pp. 326–327) shows the quantity of nitrogen, pure ash, and each ash-constituent, *per* 1000 *dry matter of produce* (grain, straw, and total) over the first eight, the second eight, and the sixteen years respectively, for each of the three plots.

It is difficult to say whether the first eight or the second eight seasons were on the average the more favourable for the crop. The first eight included perhaps more fairly good, and one or two very good seasons, but two very bad ones; whilst the second eight included the best season of the sixteen—indeed of the forty up to the present time, some others of more than average favourable character, and only one exceptionally bad one. Under these circumstances, farmyard manure, with its annual accumulation, yielded more grain, more straw, and considerably more of both nitrogen and total mineral matter, over the second than over the first eight years. Without manure, there was almost identically the same amount of grain, rather less straw, and rather less both of nitrogen and of mineral matter, over the second eight years. With ammonium-salts alone, with great relative deficiency of mineral supply, there was less corn, less straw, less mineral matter, and in a more marked degree less nitrogen in the crops, over the second eight years. It is to be observed that there was this deficiency of nitrogen in the crop over the later period, notwithstanding a great excess was annually supplied by manure.

The average quantities of total mineral constituents yielded per acre per annum over the sixteen years, on the three plots, were as follows:—

	In grain. lbs.	In straw. lbs.	Total. lbs.
By farmyard manure	36·3	201·1	237·4
Without manure	16·6	89·5	106·1
With ammonium-salts alone..	23·0	119·2	142·2

Thus, considerably more total mineral matter is taken up under the

influence of the ammonium-salts than without manure, but more than twice as much is taken up under the influence of farmyard manure as without manure. The last three columns of Table IV show a considerable increase in the amount of every constituent taken up under the influence of the ammonium-salts, and a still greater increase (excepting of soda) with the farmyard manure. The greatest *proportional* increase of constituents taken up on the ammonium-salts plot is in the lime, potash, magnesia, soda, sulphuric acid, and chlorine, and the least in phosphoric acid. With farmyard manure, by far the greatest increase is in the potash, which is more than two and a half times as much as without manure; there is also about twice as much magnesia, and more than twice as much lime, phosphoric acid, sulphuric acid, soda, and silica, and nearly four times as much chlorine.

Comparing on each plot the yield over the second eight years with that over the first eight, without manure the produce of grain contains nearly identical amounts of each ash-constituent over the two periods; but even showing a tendency to excess in magnesia, phosphoric acid, and silica, over the second period. The result is, however, different with the straw and total produce; both of which show more or less deficiency of every constituent excepting lime, which increases considerably, whilst ferric oxide and soda also show a tendency to increase. Deficiency in the straw, and with it in the total produce, that is, in the amount taken up and retained by the entire plant, or rather crop, is indication of deficient source, notwithstanding there may be no falling off in the contents of the grain.

With farmyard manure, with its excessive supply, there is over the second period compared with the first, more or less increase in every constituent in grain, in straw, and in total produce, with the single exception of sulphuric acid, which is very slightly in relative defect in the straw and total produce over the second period. In the grain, the constituents in most marked increased amount are the typical ones potash and phosphoric acid; in the straw, they are potash and silica; and in total produce, potash, phosphoric acid, and silica.

With ammonium-salts alone for so many years in succession, there is, over the second period, in the grain, only slight deficiency of potash and magnesia, a greater deficiency of phosphoric acid, and a tendency to increase in lime, sulphuric acid, and silica. In the straw and total produce, however, there is more marked deficiency in every constituent excepting sulphuric acid; and it is the most marked in the potash, the phosphoric acid, the chlorine, and the silica; the chlorine especially, although it is liberally supplied in the ammonium chloride.

That chlorine, and other constituents of possibly little other use than as carriers, may be taken up and returned to the soil, especially under certain conditions of weather, would seem not improbable. The

TABLE IV.

Average Amounts, *per Acre*, of Grain, Straw, Total Produce, Nitrogen, Ash-Constituents, and Total Ash (pure), over the First Eight, the Second Eight, and the Sixteen years, under each of the Three Conditions as to Manuring.

	Plot 2. Farmyard manure.		Plot 3. Unmanured.		Plot 10*a*. Ammonium salts alone.		16 years, 1848—'63.		
	First 8 years, 1848—'55.	Second 8 years, 1856—'63.	First 8 years, 1848—'55.	Second 8 years, 1856—'63.	First 8 years, 1848—'55.	Second 8 years, 1856—'63.	Plot 2. Farmyard manure.	Plot 3. Unmanured.	Plot 10*a*. Ammonium salts alone.
Grain to 100 straw	56·1	60·8	58·2	60·9	56·5	58·0	58·6	59·5	57·2
Weight per bushel of grain, lbs.	60·1	59·8	57·8	57·0	58·1	56·0	60·0	57·4	57·1
Quantities per Acre—Grain, lbs.									
Fresh produce	1929	2380	990	990	1578	1471	2154	990	1524
Dry matter	1608	2000	823	826	1319	1239	1804	825	1279
Nitrogen	29·2	37·0	15·9	15·4	29·6	25·3	33·1	15·7	27·5
Ash-constituents. Ferric oxide	0·28	0·31	0·16	0·17	0·20	0·21	0·30	0·16	0·20
Lime	0·84	1·03	0·47	0·47	0·83	0·84	0·94	0·47	0·84
Magnesia	3·59	4·50	1·68	1·75	2·55	2·41	4·04	1·72	2·48
Potash	10·17	12·73	5·48	5·45	7·97	7·43	11·45	5·46	7·70
Soda	0·20	0·23	0·10	0·11	0·12	0·12	0·22	0·10	0·12
Phosphoric anhydride	16·68	20·98	8·13	8·42	11·57	10·27	18·83	8·28	10·92
Sulphuric anhydride	0·27	0·27	0·20	0·21	0·41	0·53	0·27	0·21	0·47
Chlorine	0·01	0·01	0·01	0·01	0·03	0·09	0·01	0·01	0·06
Silica	0·26	0·29	0·15	0·21	0·22	0·31	0·27	0·18	0·26
Total	32·30	40·35	16·38	16·80	23·90	22·21	36·33	16·59	23·05
Deduct O = Cl	—	—	—	—	0·01	0·02	—	—	0·01
Total	32·30	40·35	16·38	16·80	23·89	22·19	36·33	16·59	23·04
Quantities per Acre—Straw, lbs.									
Fresh produce	3442	3913	1701	1626	2790	2536	3677	1663	2663

Total	32·30	40·35	16·38	16·80	23·89	22·19	36·33	16·59	23·04

Quantities per Acre—Straw, lbs.

Fresh produce	3442	3913	1701	1626	2790	2536	3677	1663	2663
Dry matter	2858	3307	1405	1375	2338	2141	3082	1390	2240
Nitrogen	13·7	13·3	7·6	6·5	18·5	11·8	13·5	7·0	15·1
Ash-constituents. Ferric oxide	0·98	1·07	0·72	0·75	0·75	0·71	1·02	0·73	0·73
Lime	7·87	8·51	2·97	3·93	7·22	7·02	8·19	3·45	7·12
Magnesia	3·01	3·04	2·30	1·46	2·27	1·95	3·03	1·88	2·11
Potash	33·22	40·18	13·89	11·96	21·46	17·57	36·70	12·93	19·52
Soda	0·99	1·02	0·47	0·51	1·52	1·17	1·00	0·49	1·34
Phosphoric anhydride	7·51	7·59	3·77	2·96	3·76	3·53	7·55	3·36	3·65
Sulphuric anhydride	5·98	5·84	2·83	2·73	4·62	4·78	5·91	2·78	4·70
Chlorine	5·75	6·93	1·78	1·58	4·30	2·72	6·34	1·68	3·51
Silica	120·45	145·13	64·42	60·68	81·20	73·35	132·79	62·55	77·27
Total	185·76	219·31	93·15	86·56	127·10	112·80	202·53	89·85	119·95
Deduct O = Cl	1·30	1·56	0·40	0·36	0·97	0·62	1·43	0·38	0·79
Total	184·46	217·75	92·75	86·20	126·13	112·18	201·10	89·47	119·16

Quantities per Acre, Total Produce (Grain and Straw), lbs.

Fresh produce	5371	6293	2691	2616	4368	4007	5831	2653	4187
Dry matter	4466	5307	2228	2201	3657	3380	4886	2215	3519
Nitrogen	42·9	50·3	23·5	21·9	48·1	37·1	46·6	22·7	42·6
Ash-constituents. Ferric oxide	1·26	1·38	0·88	0·92	0·95	0·92	1·32	0·89	0·93
Lime	8·71	9·54	3·44	4·40	8·05	7·86	9·13	3·92	7·96
Magnesia	6·60	7·54	3·98	3·21	4·82	4·36	7·07	3·60	4·59
Potash	43·39	52·91	19·37	17·41	29·43	25·00	48·15	18·39	27·22
Soda	1·19	1·25	0·57	0·62	1·64	1·29	1·22	0·59	1·46
Phosphoric anhydride	24·19	28·57	11·90	11·38	15·33	13·80	26·38	11·64	14·57
Sulphuric anhydride	6·25	6·11	3·03	2·94	5·03	5·31	6·18	2·99	5·17
Chlorine	5·76	6·94	1·79	1·59	4·33	2·81	6·35	1·69	3·57
Silica	120·71	145·42	64·57	60·89	81·42	73·66	133·06	62·73	77·58
Total	218·06	259·66	109·53	103·36	151·00	135·01	238·86	106·44	143·00
Deduct O = Cl	1·30	1·56	0·40	0·36	0·98	0·64	1·43	0·38	0·80
Total	216·76	258·10	109·13	103·00	150·02	134·37	237·43	106·06	142·20

TABLE V.

Quantities of Nitrogen, Ash-Constituents, and Total Ash (pure), *per* 1000 *Dry Matter of Produce* (Grain, Straw, and Total) over the First Eight, the Second Eigh', and the Sixteen Years, under each of the Three Conditions as to Manuring.

	Plot 2. Farmyard manure.		Plot 3. Unmanured.		Plot 10*a*. Ammonium salts alone.		16 years, 1848—'63.		
	First 8 years, 1848—'55.	Second 8 years, 1856—'63.	First 8 years, 1848—'55.	Second 8 years, 1856—'63.	First 8 years, 1848—'55.	Second 8 years, 1856—'63.	Plot 2. Farmyard manure.	Plot 3. Unmanured.	Plot 10*a*. Ammonium salts alone.
Grain to 100 straw	56·1	60·8	58·2	60·9	56·5	58·0	58·6	59·5	57·2
Weight per bushel of grain, lbs.	60·1	59·8	57·8	57·0	58·1	56·0	60·0	57·4	57·1

Per 1000 *Dry Matter of Grain.*

Fresh produce	1200	1190	1203	1199	1196	1187	1194	1200	1191
Nitrogen	18·2	18·5	19·3	18·6	22·4	20·4	18·3	19·0	21·5
Ash-constituents. Ferric oxide	0·17	0·16	0·19	0·21	0·15	0·16	0·16	0·20	0·16
Lime	0·52	0·51	0·57	0·57	0·63	0·68	0·52	0·57	0·65
Magnesia	2·24	2·25	2·05	2·12	1·93	1·94	2·24	2·08	1·93
Potash	6·32	6·36	6·66	6·59	6·05	6·00	6·35	6·62	6·02
Soda	0·12	0·12	0·12	0·13	0·09	0·10	0·12	0·13	0·10
Phosphoric anhydride	10·38	10·49	9·88	10·20	8·77	8·29	10·44	10·03	8·54
Sulphuric anhydride	0·17	0·14	0·25	0·25	0·31	0·43	0·15	0·25	0·37
Chlorine	0·01	0·01	0·01	0·01	0·02	0·07	0·01	0·01	0·04
Silica	0·16	0·14	0·18	0·26	0·16	0·25	0·15	0·22	0·21
Total	20·09	20·18	19·91	20·34	18·11	17·92	20·14	20·11	18·02
Deduct O = Cl	—	—	—	—	—	0·02	—	—	0·01
Total	20·09	20·18	19·91	20·34	18·11	17·90	20·14	20·11	18·01

Per 1000 *Dry Matter of Straw.*

Total	20·09	20·18	19·91	20·34	18·11	17·90	20·14	20·11	18·01

Per 1000 *Dry Matter of Straw.*

Fresh produce	1204	1183	1211	1182	1193	1185	1193	1196	1189
Nitrogen	4·8	4·0	5·4	4·7	7·9	5·5	4·4	5·0	6·7
Ash-constituents. Ferric oxide	0·34	0·32	0·51	0·54	0·32	0·33	0·33	0·53	0·33
Lime	2·75	2·57	2·11	2·86	3·08	3·28	2·66	2·48	3·18
Magnesia	1·05	0·92	1·63	1·06	0·97	0·91	0·98	1·35	0·94
Potash	11·62	12·15	9·89	8·70	9·18	8·21	11·91	9·30	8·71
Soda	0·35	0·31	0·33	0·38	0·65	0·55	0·32	0·35	0·60
Phosphoric anhydride	2·63	2·30	2·69	2·15	1·61	1·65	2·45	2·42	1·63
Sulphuric anhydride	2·09	1·77	2·01	1·98	1·98	2·23	1·92	2·00	2·10
Chlorine	2·01	2·10	1·27	1·15	1·84	1·27	2·06	1·21	1·57
Silica	42·15	43·88	45·85	44·13	34·73	34·26	43·08	45·00	34·49
Total	64·99	66·32	66·29	62·95	54·36	52·69	65·71	64·64	53·55
Deduct O = Cl	0·45	0·47	0·28	0·26	0·41	0·29	0·46	0·27	0·35
Total	64·54	65·85	66·01	62·69	53·95	52·40	65·25	64·37	53·20

Per 1000 *Dry Matter of Total Produce* (*Grain and Straw*).

Fresh produce	1203	1186	1208	1189	1194	1186	1193	1198	1190
Nitrogen	9·6	9·5	10·6	10·0	13·2	11·0	9·5	10·3	12·1
Ash-constituents. Ferric oxide	0·28	0·26	0·39	0·42	0·26	0·27	0·27	0·41	0·27
Lime	1·95	1·80	1·54	2·00	2·20	2·33	1·87	1·77	2·26
Magnesia	1·48	1·42	1·79	1·46	1·32	1·29	1·45	1·62	1·30
Potash	9·71	9·97	8·70	7·91	8·05	7·40	9·85	8·30	7·74
Soda	0·27	0·24	0·26	0·28	0·45	0·38	0·25	0·27	0·42
Phosphoric anhydride	5·42	5·38	5·34	5·17	4·19	4·08	5·40	5·26	4·14
Sulphuric anhydride	1·40	1·15	1·36	1·33	1·37	1·57	1·27	1·35	1·47
Chlorine	1·29	1·31	0·80	0·72	1·19	0·83	1·30	0·76	1·01
Silica	27·03	27·40	28·98	27·67	22·26	21·79	27·23	28·32	22·03
Total	48·83	48·93	49·16	46·96	41·29	39·94	48·89	48·06	40·64
Deduct O = Cl	0·29	0·30	0·18	0·16	0·27	0·19	0·29	0·17	0·23
Total	48·54	48·63	48·98	46·80	41·02	39·75	48·60	47·89	40·41

experiments of Anderson and ourselves with beans show a considerable reduction in the amount of mineral matter in the crop of a given area during the last few weeks, but in the case of this crop there is a considerable fall of leaf at this period. Dr. Anderson's results with wheat do not show such reduction, either of total mineral matter, potash, phosphoric acid, or silica. E. Wolff's experiments with potatoes showed considerable reduction in the amounts of nitrogen, total ash, lime, magnesia, and chloride of sodium, during the last five weeks, but there was also considerable loss of total dry substance. His experiments with mangel-wurzel, red clover, lucerne, and rape showed, with immaterial exceptions, considerable gain of all constituents to the end of the period quoted, when, however, such crops would not have ripened. In one experiment with barley, there was gain of every constituent to the end; in a second there was gain in all excepting potassium chloride, and potash, both of which showed a loss in the last stage; and in a third there was considerable reduction in total ash, chiefly in magnesia, potassium chloride, and potash. In two experiments with oats, there was gain in total ash, but considerable loss of potash. In an experiment with wheat, though there was a gain in total ash, there was a considerable reduction of potash. In experiments on barley, by Schéven, there was gain of nitrogenous, non-nitrogenous, and total dry substance to the end, also gain of total ash, phosphoric acid, soda, and chlorine; but reduction in potash, lime, and magnesia. In experiments with barley, Bretschneider found gain in total dry matter, nitrogen, total ash, and most individual ash-constituents to the end, but during ripening a slight reduction of potash and chlorine was indicated. According to Joulie's experiments, there is a considerable reduction in the amount, especially of potash, in the total wheat-plant during the seed-forming and ripening periods. Marie-Davy concluded that during the ripening period plants expel superfluous matters by their roots. Pierre, in experiments with rape, found a reduction in the amounts of nitrogen, and most ash-constituents, excepting phosphoric acid, in the later stages; but he notes that leaves had fallen. In his experiments with wheat, the results were very similar. In experiments with oats, Arendt did not find any appreciable reduction either in total ash, or in ash-constituents, excepting soda. In experiments with wheat, Dehérain found no reduction until the crop was ripe, but a good deal afterwards; and here the question arises whether there was not loss by birds, or otherwise than by excretion by the plant. In his experiments with oats, the results were irregular, owing to unfavourable weather. Upon the whole, it would seem that satisfactory evidence is still wanting on the point; and it is probable that the result will be considerably influenced by the conditions of the weather.

Recurring to the results as to the yield *per acre* of the several con-

stituents (in grain and straw) over the first and second half of the sixteen years, as given in Table IV (pp. 324–325), without manure there is indicated a comparatively small relative exhaustion of both potash and phosphoric acid, and with ammonium-salts a greater exhaustion of both.

Table V (pp. 326–327), which gives the amount of each constituent *per* 1000 *dry substance* of grain, straw, and total produce, shows the degree in which the composition is affected by the excess or deficiency of supply.

Taking the mean result for the sixteen years in each case, 1000 dry substance of grain shows a rather higher proportion of nitrogen without manure than with farmyard manure, and higher still with ammonium-salts alone. It shows almost identical amounts of total mineral constituents under the influence of full supply of them by farmyard manure, and of exhaustion of both nitrogen and mineral constituents without manure. There is, however, a considerable deficiency under the very abnormal exhaustion of mineral constituents, when ammonium-salts alone are used for so many years in succession. The dry substance of the unmanured grain contains a rather higher proportion of potash, rather less magnesia, and less phosphoric acid, than that grown by farmyard manure. The relative deficiency in the dry substance of the grain grown by ammonium-salts is partly in potash, but mainly in phosphoric acid, which is only in small part compensated by an increased amount of sulphuric acid. Magnesia is also in slight relative defect.

The composition of the straw, which much more directly indicates relative supply or exhaustion, shows much wider variation under the three different conditions as to manuring. Compared with the straw grown with farmyard manure, that grown without manure contains, per 1000 dry substance, considerably less potash, but otherwise there is but little difference, excepting that it contains notably less chlorine and more silica. With ammonium-salts alone, there is a still greater decrease in the amount of potash in the dry substance of the straw, partly compensated by more lime. There is also considerably less phosphoric acid, but rather more sulphuric acid, and there is much less silica than either with farmyard manure or without manure.

Comparing the average composition of the produce of the second eight years with that of the first, with farmyard manure, the mineral composition of the dry substance of the grain is almost absolutely identical over the two periods. Without manure, again, it is very nearly so, the figures showing, however, a tendency to a rather lower proportion of potash over the latter half of the total period, with at the same time slightly more magnesia, and also more phosphoric acid; conditions which are indicative of less perfect maturation, that is, less flour in proportion to bran. With ammonium-salts, the mineral com-

position of the grain, though showing, compared with that of the other plots, a marked deficiency in potash and magnesia, and especially in phosphoric acid, shows very little difference comparing the second eight years with the first. So far as the bases are concerned, the average proportion in the dry substance of the grain is almost identical over the two periods; but there is an obvious tendency over the later period to decrease in phosphoric acid, and with this to increase in sulphuric acid and in silica.

The composition of the dry substance of the straw, which has been seen to vary considerably as between plot and plot, varies also much more than does that of the grain over the two periods, but still comparatively little. With farmyard manure, the chief difference is that there is a somewhat larger proportion of potash and silica, and somewhat less phosphoric acid and sulphuric acid over the second period, differences probably due to season and character of growth depending thereon, rather than to soil supply independently of these. Without manure, the chief indication is a relative deficiency of potash and magnesia, partly compensated by more lime, also a deficiency of phosphoric acid over the second period. With ammonium-salts alone, the most marked difference is a relative deficiency of potash over the later period.

Thus, although it has been shown that there is much wider range of variation in the mineral composition of wheat-grain according to season than according to manure, it is seen that there is nevertheless an obvious difference in the average composition of the grain under the three very different conditions as to manuring; but with each there is almost identical average composition over the first and second half of the period of sixteen years. The grain grown by the ammonium-salts alone shows exhaustion both of potash and phosphoric acid, but especially the latter. The condition of exhaustion here is, however, quite abnormal, and the results as a whole point to great uniformity in the mineral composition of the grain under varying conditions as to manure, provided only that it is perfectly and normally ripened. It will be seen, too, that the lowest average proportion of nitrogen is in the grain grown by farmyard manure, notwithstanding its liberal supply of it, again indicating that the composition, and especially high or low percentage of nitrogen, is much more dependent on maturation than on full or limited supply by the soil. The next series of results will further illustrate the influence of season and manuring on the composition of the wheat crop in selected seasons, and with a greater variety of manuring.

Second Series of Analyses.

This series includes the results obtained under nine different con-

ditions as to manuring, each in two unfavourable and in two favourable seasons for the crop:—

The conditions as to manuring were:—

Plot 2. Farmyard manure, every year.
Plot 3. Unmanured, every year.
Plot 5*a*. Mixed mineral manure,* alone.
Plot 7*a*. Mixed mineral manure,* and ammonium-salts.†
Plot 10*a*. Ammonium-salts, alone.
Plot 11*a*. Ammonium-salts and superphosphate of lime.‡
Plot 12*a*. Ammonium-salts, superphosphate, and sulphate of soda.§
Plot 13*a*. Ammonium-salts, superphosphate, and sulphate of potash.‖
Plot 14*a*. Ammonium-salts, superphosphate, and sulphate of magnesia.¶

It will be seen that, besides the conditions of manuring to which the first series of analyses relates, this series includes the results obtained on six other plots with widely different, but strictly comparable, conditions of mineral or ash-constituent supply. Thus, we have ammonium-salts alone; the same with superphosphate; the same with superphosphate and soda-salt; the same with superphosphate and potash-salt; the same with superphosphate and magnesia-salt; and the same with superphosphate, potash-, soda-, and magnesia-salt. The seasons selected were 1852, 1856, 1858, and 1863.

1852 was the ninth season from the commencement of the experiments, and the first of the twelve which comprise the four to which the series of analyses now under consideration relates. The winter had been favourable upon the whole; but the spring was dry, cold, and backward; the early summer was rainy and cold; and the maturing period variable, with a good deal of hot weather, but some heavy storms. Without manure, the produce of grain was the lowest that

* The mixed mineral manure was composed per acre as follows:—1852–1858, sulphate of potash 300 lbs., sulphate of soda 200 lbs., sulphate of magnesia 100 lbs.; 1859 and since, sulphate of potash 200 lbs., sulphate of soda 100 lbs., sulphate of magnesia 100 lbs.; also superphosphate of lime made as described below.

† Ammonium-salts, in all cases 200 lbs. sulphate, and 200 lbs. muriate of ammonia of commerce, per acre.

‡ Superphosphate of lime (per acre), in all cases made from bone-ash 200 lbs., sulphuric acid (sp. gr. 1·7) 150 lbs., and water.

§ Sulphate of soda, 500 lbs. per acre 1852–1858; two-thirds as much 1859 and afterwards.

‖ Sulphate of potash, 300 lbs. per acre 1852–1858; 200 lbs. 1859 and afterwards.

¶ Sulphate of magnesia, 420 lbs. per acre 1852–1858; two-thirds as much (280 lbs.), 1859 and afterwards.

had been obtained so far, and below the average of the first 20 years. Under the influence of ammonium-salts, whether alone or in conjunction with mineral manures, the produce of grain was very much, and that of straw considerably, below the average obtained by such manures. Finally, the proportion of grain to straw, and the weight per bushel of the grain, were very low.

1856 was the thirteenth season of the experiments. The winter had been mild upon the whole; the early spring was dry and cold, and the remainder cold and wet, the early summer was cold and changeable, then came a short interval of fine and hot weather, succeeded, about the ripening period, by very heavy rains, and prevailing low temperatures. The harvest was also wet and unfavourable. With these conditions of season, the quantity of grain per acre was, excepting without manure, fully equal to, and that of the straw rather over, the average of the 12 years which comprise the four now under consideration. The crops were, however, unevenly and badly ripened, and the proportion of grain to straw, and the weight per bushel of the grain, were low. The season was therefore, upon the whole, not unfavourable to quantity of produce, but it was unfavourable for the full development and maturation of the grain.

1858 was the fifteenth season from the commencement. During the winter, spring, and summer there was, upon the whole, much less than the usual amount of rain; though in February, April, May, and July, there were fair amounts. Throughout the summer, the air was generally drier than usual for the period, and the temperature was generally above the average throughout the spring and summer months, whilst June was unusually hot. Early in the summer, the promise was of great luxuriance, but the warm and dry weather of June checked this tendency, and brought on early maturity; and the harvest weather was favourable. Accordingly, the quantity of straw was generally below the average with parallel conditions as to manuring; but that of the grain was generally above it, especially with high manuring. The proportion of grain to straw was thus above the average, and the weight per bushel of the grain was also above the average.

1863 was the twentieth season of the experiments. The winter and early spring were extremely mild, the plant came early forward, and the rains, though sparing upon the whole, came when needed, whilst the temperature of the summer, though seldom high, was (excepting some night frosts in July) generally sufficient, and the condition of the atmosphere was otherwise favourable. The characters of the season were such as to contribute to a lengthened and almost uninterrupted course of accumulation; and this, the twentieth wheat crop in succession on the same land, was not only the best up to that time

obtained in quantity both of grain and straw, but it is the best obtained during the 40 years to 1883, inclusive. It was also nearly the best as to quality of grain. This extraordinary result was due to almost unchecked growth from the first appearance of the plant above ground, up to the time of harvest, rather than to any extraordinary characteristics at any one or more particular period.

Thus, of the four seasons selected, 1852 was very bad, both as to quantity and quality of produce; 1856 gave fairly average quantity of both grain and straw, but the crop was unevenly ripened, and the weight per bushel was low; 1858 yielded only a moderate amount of total produce, but a more than average proportion and amount of grain, and the weight per bushel was also above the average; lastly, 1863 was the most productive season of the forty of the experiments, as to quantity both of straw and of grain; the weight per bushel of grain was also considerably above the average.

The analytical results (excluding sand and charcoal), are given in detail in Appendix Table X; in Appendix Table XI, the constituents are calculated *per* 1000 *dry substance*, instead of per 100 of ash; and in Appendix Table XII, the quantity of each constituent in the produce *per acre* is given. Referring to these Tables for the study of the details, it will be convenient here to discuss the main bearings of the results by reference to a series of Summary Tables.

In Table VI (p. 334), the mean percentage of selected constituents in the pure ash (of grain and straw respectively), of the nine differently manured plots collectively, is given for each of the four seasons. Thus the effects of season, independently of manure, are shown. By the side of these results are given, as before, the general characters of the produce of each season, as indicated by the average weight per bushel of the grain on the nine plots, the proportion of grain to straw, the amount of total produce (grain and straw) per acre, and finally the mean percentage of nitrogen, and of total mineral matter (or ash) in the dry substance.

It is seen that, as indicated by the weight per bushel of the dressed grain, the quality of the grain was the lowest in the first, and the highest in the last of the four seasons, rising from year to year, taking the seasons in their chronological order. The first two years show lower than average, and the last two higher than average quality. The last two also show very much the higher proportion of grain to straw, that is, a very much higher seed-forming tendency. There can be no doubt, therefore, that so far as quality of produce is concerned the last two seasons were far superior to the first two, which were in fact very bad seasons; whilst the two later seasons were much better, and the last of the four one of very high quality. As to quantity of grain too, there is an increase from the first to the fourth

TABLE VI.

General Characters of the Produce, and *Mean Percentage Composition of the Pure Ash*, in each of the Four Seasons. Means of Nine Differently Manured Plots in each Season.

Harvests.	Weight per bushel of grain, lbs.	Grain to 100 straw.	Produce per acre, lbs.	Per cent. in dry matter.		Per cent. in pure ash.					
				Nitrogen.	Ash (pure).	Lime.	Magnesia.	Potash.	Phosphoric acid.	Sulphuric acid.	Silica.
					Grain.						
1852	56·8	46·8	1390	2·02	1·96	3·17	12·7	28·4	52·9	0·42	0·92
1856	57·4	53·9	1832	1·98	1·92	2·92	11·3	30·1	52·8	0·68	1·00
1858	61·4	66·4	1993	1·96	1·96	3·10	10·4	33·2	50·3	1·06	0·73
1863	62·6	65·8	2761	1·66	1·75	3·01	10·9	33·1	49·9	1·26	0·66
					Straw.						
1852	56·8	46·8	2967	0·59	6·10	4·80	1·72	12·0	3·39	2·44	72·7
1856	57·4	53·9	3397	0·39	5·27	5·00	1·45	14·7	3·48	3·22	68·5
1858	61·4	66·4	3003	0·46	5·59	5·65	1·71	19·8	3·08	5·03	59·9
1863	62·6	65·8	4197	0·32	5·65	5·48	1·72	17·2	2·55	3·47	65·7

season, the last yielding about twice as much as the first, and about one and half time as much straw.

Coincidently with these general agricultural characters of great superiority in the produce of 1863, there is by far the lowest average percentage of both nitrogen and mineral matter (ash), in the dry substance of the grain. In the dry substance of the straw, the percentage of mineral matter is not specially low, but that of the nitrogen is very low, both actually and relatively. The description of the seasons already given shows that the fairly good season of 1858 was one of early but checked, and finally, limited luxuriance, with high seed-forming tendency, in proportion to the amount of plant; whilst that of 1863 was one of very great luxuriance throughout the growing period, with very high seed-forming tendency supervening. It will afterwards be seen, indeed, that the total crop of 1863 contained about one and a half time as much mineral matter per acre, and also considerably more nitrogen, than that of either of the other seasons; yet the percentage of both was much lower in the grain, and that of the nitrogen lower also in the straw, than in the produce of either of the other years. There is here again evidence that with favourable maturation there is low percentage of both mineral matter and nitrogen; that is, favourable maturation means the greater accumulation of non-nitrogenous organic substances—carbohydrates, and especially starch—the result necessarily being a lowering of the proportion, though not of the actual amount, of both the nitrogenous and the mineral constituents.

Turning to the composition of the ash, Table VI (p. 334) shows a considerably higher percentage of potash, and a considerably lower percentage of phosphoric acid, in the ash of the grain of the two seasons of better quality. At the same time there is a tendency to lower percentages of magnesia with the higher percentages of potash, and to higher percentages of sulphuric acid with the lower percentages of phosphoric acid, but by no means in compensating degree. The straw-ashes also show considerably higher percentages of potash, low percentages of phosphoric acid, and higher of sulphuric acid, in the better seasons. But it has before been observed that the ash of the straw, in a much greater degree than does that of the grain, contains, besides the constituents that may be essential to its own formations, a variable amount of what may be called migratory matters, the quantities of which depend on the one hand on the quantities taken up from the soil during the periods of accumulation, and on the other on the characters of the maturing period, which influence the amounts stored up in the seed.

The variations in the average percentage composition of the ash itself in the several seasons, as shown in Table VI, though instruc-

TABLE VII.

General Characters of the Produce, and Mean Quantity of Nitrogen, Ash, and each Ash-Constituent, *per* 1000 *Dry Matter of Produce*. Mean of Nine Differently Manured Plots in each Season.

Harvests.	Weight per bushel of grain, lbs.	Grain to 100 straw.	Dry matter per acre, lbs.	Per 1000 dry matter.		Ash-constituents per 1000 dry matter.					
				Nitrogen.	Ash (pure).	Lime.	Magnesia.	Potash.	Phosphoric acid.	Sulphuric acid.	Silica.
Grain.											
1852	56·8	46·8	1161	20·2	19·6	0·62	2·49	5·54	10·38	0·08	0·18
1856	57·4	53·9	1526	19·8	19·2	0·56	2·18	5·76	10·18	0·12	0·19
1858	61·4	66·4	1670	19·6	19·6	0·60	2·05	6·51	9·91	0·19	0·14
1863	62·6	65·8	2335	16·6	17·5	0·53	1·91	5·84	8·72	0·23	0·12
Straw.											
1852	56·8	46·8	2467	5·9	61·0	2·98	1·02	7·45	2·06	1·49	44·2
1856	57·4	53·9	2839	3·9	52·7	2·62	0·76	7·97	1·80	1·66	36·0
1858	61·4	66·4	2550	4·6	55·9	3·05	0·92	11·54	1·70	2·71	33·1
1863	62·6	65·8	3493	3·2	56·5	3·18	0·98	10·20	1·38	1·91	36·4

tive, do not clearly indicate the variations in the mineral composition of the produce. These are best shown in Table VII (p. 336), which gives, besides the general agricultural characters of the produce as before, the average amounts for each season, of nitrogen, of total ash, and of each of the selected ash-constituents, *per* 1000 *dry matter of the produce*, grain and straw respectively:—

Thus, notwithstanding the much higher percentage of potash in the ash of the grain of the two good seasons than in that of the two bad ones, its proportion in the dry substance of the grain of the best season, 1863, is, owing to its small amount of total ash, little above that in the dry substance of the grain of the two bad seasons, with their higher amounts of total ash. The dry substance of the grain of the other good season, 1858, with its less perfect ripening, and higher proportion of total ash, shows, however, a high proportion of potash in the dry substance.

The most striking difference in the average mineral composition of the grain in the four seasons is the very much lower proportion of phosphoric acid, and with this a lower proportion of magnesia also, in the dry substance of the best matured grain—that of 1863. These are characteristics of a less proportion of bran to flour—in other words, of a greater accumulation of starch in the ripening. The variation in the mineral composition is thus coincident with, and dependent on, variation in that of the organic substance due to season.

After what has been said of the circumstances affecting the composition of the straw-ash, it is unnecessary to consider in any detail the differences in the proportion of the several mineral constituents in the dry substance of the straw in the different seasons. It may be noted, however, that, in the better seasons, the amount of potash remaining in the straw is much greater, that of phosphoric acid is less, and that of sulphuric acid greater, in proportion to a given quantity of dry substance of the straw.

The summary Table VIII (p. 338) shows the mean yield per acre of the produce, and of its constituents, on the nine differently manured plots in each of the four seasons:—

It is thus seen that under identical conditions as to manuring, there was about twice as much grain, nearly one and a half time as much straw, and more than one and a half time as much total produce, in the best as in the worst of the four seasons. Of nitrogen in the total produce, the average amount per acre was only 38 lbs. in 1852, but 50·1 lbs. in 1863; whilst of the less total amount in the crop in 1852, a considerably larger actual quantity remained in the straw. In fact, of the total nitrogen in the crop, in 1852, 38·4 per cent., in 1856, 27·1, in 1858, 26·2, and in 1863, only 22·6 per cent. remained in the straw.

TABLE VIII.

General Characters of the Produce, and Average Quantities *per Acre*, of Grain, Straw, Total Produce, Nitrogen, Ash, and of Selected Ash-Constituents, in each of the Four Seasons. Mean of Nine Differently Manured Plots in each Season.

Harvests.	Weight per bushel of grain, lbs.	Grain to 100 straw.	Produce per acre, lbs.	Per acre, lbs.		Ash-constituents per acre, lbs.					
				Nitrogen.	Ash (pure).	Lime.	Magnesia.	Potash.	Phosphoric acid.	Sulphuric acid.	Silica.
Grain.											
1852	56·8	46·8	1390	23·4	22·7	0·72	2·89	6·4	12·0	0·09	0·21
1856	57·4	53·9	1832	30·2	29·4	0·86	3·32	8·8	15·5	0·19	0·29
1858	61·4	66·4	1993	32·7	32·8	1·00	3·42	10·9	16·6	0·32	0·23
1863	62·6	65·8	2761	38·8	40·9	1·24	4·47	13·6	20·4	0·53	0·27
Straw.											
1852	56·8	46·8	2967	14·6	150·6	7·34	2·52	18·4	5·1	3·68	109·1
1856	57·4	53·9	3397	11·2	149·7	7·43	2·16	22·6	5·1	4·72	102·1
1858	61·4	66·4	3003	11·6	142·5	7·77	2·35	29·4	4·3	6·92	84·4
1863	62·6	65·8	4197	11·3	197·3	11·10	3·43	35·6	4·8	6·68	127·2
Total.											
1852	56·8	46·8	4357	38·0	173·3	8·06	5·41	24·8	17·1	3·77	109·3
1856	57·4	53·9	5229	41·4	179·1	8·29	5·48	31·4	20·6	4·91	102·4
1858	61·4	66·4	4996	44·3	175·3	8·77	5·77	40·3	20·9	7·24	84·7
1863	62·6	65·8	6958	50·1	238·2	12·34	7·90	49·2	25·2	7·21	127·5

Yet, with by far the largest amount accumulated in the grain in 1863, its percentage in it is much lower than in either of the other years. There is thus, with the best growing and maturing conditions, the largest amount of nitrogen taken up by the plant, the largest amount accumulated in the grain, and the lowest percentage of it in the grain.

Again, under equal conditions as to supply by manure, one and a third time as much of total mineral, or ash-constituents, is stored up in the total crop in the season of highest luxuriance and highest maturation, as in either of the others; whilst the percentage of ash in the dry substance of the grain is lower than in either of the other years. There is also more of each of the mineral constituents enumerated (excepting silica), taken up, with the same supply by manure, in the two better than in the two worse seasons; and comparing the best season with the worst there is about one and a half time as much lime, magnesia, and phosphoric acid, and about twice as much potash and sulphuric acid, taken up in the season of most favourable growth and maturation. Yet, as Table VII (p. 336) shows, the proportion of lime, magnesia, and phosphoric acid was lower, and that of the potash nearly as low, in the grain of the large and well-matured produce.

In these facts as to the nitrogen and the ash-constituents, there is again striking evidence of the much greater influence of season than of manuring on the composition of a ripened plant, and especially of its final product—the seed. The extent, and the limits, of the effects of manure, or of exhaustion, on the composition of wheat-grain and wheat-straw will be more clearly brought to view in the next illustrations.

In the first place, Table IX (p. 340) shows a not very wide range of difference in the weight per bushel of the grain grown under such very wide differences as to manure, but all under equal season influences. Still the differences, such as they are, are not without their significance. Without manure (Plot 3), with sluggish growth and ripening, and with ammonium-salts alone (Plot 10*a*), that is, with great mineral exhaustion, the weight per bushel is low; it is also low on Plot 11*a*, where, besides the ammonium-salts, there is superphosphate, but neither potash, soda, nor magnesia supplied. With farmyard manure (Plot 2) it is high. In the other cases—with mixed mineral manure (Plot 5*a*), the same and ammonium-salts (Plot 7*a*), ammonium-salts, superphosphate, and soda (Plot 12*a*), ammonium-salts, superphosphate, and potash (Plot 13*a*), and ammonium-salts, superphosphate, and magnesia (Plot 14*a*)—it is fairly uniform.

The percentage of nitrogen in the dry substance of the grain is fairly uniform, excepting that on Plot 5*a*, with mineral manure alone and great nitrogen exhaustion, it is low; and on Plot 10*a*, with ammonium-salts alone, and therefore great relative excess of nitrogen and deficiency of mineral constituents supplied, it is high.

TABLE IX.

General Characters of the Produce, and *Mean Percentage* of Selected Constituents *in the Pure Ash*, of the Grain and Straw, under each of the Nine Different Conditions as to Manuring. Mean Result of the Four Seasons for each Plot.

Plots.	Weight per bushel of grain, lbs.	Grain to 100 straw.	Produce per acre, lbs.	Per cent. in dry matter.		Per cent. in pure ash.					
				Nitrogen.	Ash (pure).	Lime.	Magnesia.	Potash.	Phosphoric acid.	Sulphuric acid.	Silica.
					Grain.						
2	60·6	59·1	2348	1·80	1·96	2·57	11·8	30·0	53·2	0·51	0·72
3	58·5	62·6	1005	1·85	2·01	2·71	11·0	31·3	51·7	0·85	0·97
5*a*	59·6	65·6	1169	1·74	2·02	2·82	11·0	31·4	52·1	0·67	0·90
10*a*	58·4	61·1	1713	2·08	1·75	3·76	11·5	32·0	48·9	1·69	1·01
11*a*	59·0	61·8	2107	1·92	1·85	3·83	11·2	30·3	51·3	1·02	0·90
12*a*	60·1	59·1	2394	1·83	1·86	3·12	11·1	31·5	51·4	0·90	0·72
13*a*	60·2	57·0	2338	1·85	1·86	2·92	11·1	31·7	51·5	0·73	0·72
14*a*	60·0	56·9	2411	1·87	1·85	2·94	11·4	31·1	51·7	0·85	0·68
7*a*	59·6	54·1	2464	1·87	1·88	2·79	11·8	31·5	51·5	0·50	0·84
					Straw.						
2	60·6	59·1	3972	0·38	6·59	3·92	1·55	16·8	3·30	2·83	68·3
3	58·5	62·6	1606	0·44	6·38	4·41	2·00	13·2	3·43	3·20	71·1
5*a*	59·6	65·6	1783	0·44	6·83	3·76	1·33	14·3	3·98	4·01	69·2
10*a*	58·4	61·1	2804	0·58	5·09	6·68	1·75	14·0	2·68	4·55	66·8
11*a*	59·0	61·8	3407	0·46	5·40	6·61	1·82	9·2	3·09	3·35	72·3
12*a*	60·1	59·1	4052	0·39	5·26	5·91	1·68	16·9	2·78	3·46	65·1
13*a*	60·2	57·0	4099	0·34	5·45	4·83	1·44	20·6	2·73	3·34	62·3
14*a*	60·0	56·9	4236	0·38	5·25	5·84	1·85	18·8	2·89	3·52	63·0
7*a*	59·6	54·1	4557	0·51	5·47	5·15	1·42	19·6	3·25	3·62	62·1

The percentage of total mineral matter (pure ash), is also fairly uniform, excepting that with farmyard manure (2), with purely mineral manure (5*a*), and without manure (3), it is somewhat high; and with ammonium-salts alone (10*a*), where there is very abnormal mineral exhaustion, it is very low.

A glance at the columns showing the mean percentage of the chief constituents of the ash of the grain shows a very marked uniformity under the nine very characteristically different conditions as to actual and relative mineral supply. In the potash column, for example, the only exceptions to this general uniformity are that with farmyard manure (2), and with ammonium-salts and superphosphate, but without either potash, soda, or magnesia applied (11*a*), the mean percentage is low. In the case of the farmyard manure plot, the result is obviously due to the characters of the growth and maturation, and not to deficient supply, as confirmed by the comparatively high percentage of potash in the straw-ash. In the case of 11*a*, there is doubtless great potash exhaustion, and accordingly the straw-ash also shows a very low percentage of potash; indeed a much lower percentage than on any other plot.

In the phosphoric acid column again there is, upon the whole, great uniformity. The exceptions are, that with farmyard manure (2), the percentage is very high; and with ammonium-salts alone (10*a*), where there is very abnormal exhaustion, it is very low; and consistently with this, the percentage in the straw-ash is also low. With this low amount of phosphoric acid in the ash of both the grain and the straw of Plot 10*a*, there is, in both the grain-ash and the straw-ash of this plot, the highest percentage of sulphuric acid.

The influence of supply, or exhaustion, on the amount of produce, on the amount of the different constituents taken up by the plant, on the distribution of the constituents in the grain and straw respectively, and on the composition of the dry matter of the grain and straw, will be further illustrated in Tables X and XI (pp. 342–344). It will be convenient first to consider the variations in the amounts of produce, and in the amounts and distribution of the various constituents taken up over a given area, and afterwards the composition of the dry substance produced.

In reference to the results given in Table X (pp. 342–343), it is first to be noted that the quantity of produce, both grain and straw, yielded per acre, varied exceedingly under the very different conditions as to manuring. Without manure (3), the produce was very small; with a full mineral manure, but no nitrogen supplied (5*a*), it was but little higher. Then, taking the series with a given amount of ammonium-salts annually applied, there is in every case much more produce, and much more nitrogen and mineral matter taken up,

TABLE X.

General Characters of the Produce, and the Amounts of Nitrogen, Total Mineral Matter (Ash), and each Ash-Constituent *Per Acre*, in Grain, Straw, and Total Produce. Mean Results of the Four Seasons for each Plot.

Plots.	Weight per bushel of grain. lbs.	Grain to 100 straw.	Produce per acre, lbs.	Per acre, lbs.		Ash-constituents per acre, lbs.						
				Nitrogen.	Ash (pure).	Lime.	Magnesia.	Potash.	Phosphoric acid.	Sulphuric acid.	Chlorine.	Silica.
						Grain.						
2	60·6	59·1	2348	35·4	38·5	0·98	4·48	11·6	20·4	0·22	0·02	0·27
3	58·5	62·6	1005	15·5	16·8	0·45	1·83	5·3	8·6	0·14	trace	0·16
5*a*	59·6	65·6	1169	17·0	19·7	0·55	2·16	6·2	10·2	0·13	trace	0·18
10*a*	58·4	61·1	1713	30·0	25·2	0·95	2·87	8·1	12·2	0·45	0·05	0·25
11*a*	59·0	61·8	2107	34·0	32·8	1·26	3·63	10·0	16·7	0·36	0·01	0·29
12*a*	60·1	59·1	2394	36·8	37·5	1·18	4·08	12·0	19·0	0·39	0·03	0·26
13*a*	60·2	57·0	2338	36·3	36·5	1·06	3·99	11·8	18·7	0·30	0·01	0·26
14*a*	60·0	56·9	2411	37·9	37·6	1·10	4·22	11·9	19·3	0·36	0·02	0·25
7*a*	59·6	54·1	2464	38·6	38·7	1·07	4·49	12·4	19·8	0·21	trace	0·32
						Straw.						
2	60·6	59·1	3972	12·8	219·3	8·59	3·39	36·9	7·2	6·17	6·89	149·9
3	58·5	62·6	1606	5·9	86·2	3·73	1·72	11·3	3·0	2·72	1·54	61·5
5*a*	59·6	65·6	1783	6·6	101·9	3·84	1·36	14·3	4·1	4·06	1·85	70·8
10*a*	58·4	61·1	2804	13·6	119·9	7·86	2·05	16·5	3·1	5·07	2·93	81·2
11*a*	59·0	61·8	3407	13·1	154·3	10·25	2·86	13·9	4·7	5·10	2·99	111·7
12*a*	60·1	59·1	4052	13·1	178·3	10·72	3·07	30·3	4·8	6·14	6·44	115·8
13*a*	60·2	57·0	4099	11·6	185·8	8·99	2·69	39·2	4·9	6·19	8·87	114·9
14*a*	60·0	56·9	4236	13·6	186·1	10·95	3·47	34·9	5·2	6·50	7·38	117·3
7*a*	59·6	54·1	4557	19·4	208·3	10·75	2·95	41·5	6·7	7·58	9·55	128·4

Total Produce (Grain and Straw).

2	60·6	59·1	6320	48·2	257·8	9·57	7·87	48·5	27·6	6·39	6·91	150·1
3	58·5	62·6	2611	21·4	103·0	4·18	3·55	16·6	11·6	2·86	1·54	61·7
5*a*	59·6	65·6	2952	23·6	121·6	4·39	3·52	20·5	14·3	4·19	1·85	71·0
10*a*	58·4	61·1	4517	43·6	145·1	8·81	4 92	24·6	15·3	5·52	2·98	81·5
11*a*	59·0	61·8	5514	47·1	187·1	11·51	6·49	23·9	21·5	5·46	3·00	112·0
12*a*	60·1	59·1	6446	49·9	215·8	11·90	7·15	42·3	23·8	6·53	6·47	116·1
13*a*	60·2	57·0	6437	47·9	222·3	10·05	6·68	51·0	23·6	6·49	8·88	115·2
14*a*	60·0	56·9	6647	51·5	223·7	12·05	7·69	46·8	24·5	6·86	7·40	117·5
7*a*	59·6	54·1	7021	58·0	247·0	11·82	7·44	53·9	26·5	7·79	9·55	128·7

TABLE XI.

General Characters of the Produce, and Amounts of Nitrogen, Total Ash, and of Selected Ash-Constituents *per* 1000 *Dry Matter of Grain, and of Straw.* Mean Results of the Four Seasons for each Plot.

Plots.	Weight per bushel of grain. lbs.	Grain to 100 straw.	Dry matter per acre, lbs.	Per 1000 dry matter.		Ash-constituents per 1000 dry matter.					
				Nitrogen.	Ash (pure).	Lime.	Magnesia.	Potash.	Phosphoric acid.	Sulphuric acid.	Silica.
					Grain.						
2	60·6	59·1	1963	18·0	19·6	0·50	2·28	5·93	10·38	0·11	0·14
3	58·5	62·6	836	18·5	20·1	0·54	2·19	6·30	10·35	0·17	0·19
5*a*	59·6	65·6	975	17·4	20·2	0·56	2·22	6·35	10·51	0·13	0·18
10*a*	58·4	61·1	1443	20·8	17·5	0·66	1·99	5·65	8·46	0·31	0·17
11*a*	59·0	61·8	1773	19·2	18·5	0·71	2·05	5·68	9·44	0·20	0·16
12*a*	60·1	59·1	2014	18·3	18·6	0·59	2·03	5·96	9·47	0·19	0·13
13*a*	60·2	57·0	1963	18·5	18·6	0·54	2·03	6·01	9·52	0·15	0·13
14*a*	60·0	56·9	2028	18·7	18·5	0·54	2·09	5·85	9·52	0·18	0·12
7*a*	59·6	54·1	2062	18·7	18·8	0·52	2·18	5·99	9·62	0·10	0·16
					Straw.						
2	60·6	59·1	3328	3·8	65·9	2·58	1·02	11·07	2·18	1·85	45·03
3	58·5	62·6	1351	4·4	63·8	2·88	1·27	8·34	2·19	2·01	45·55
5*a*	59·6	65·6	1492	4·4	68·3	2·57	0·91	9·60	2·74	2·72	47·46
10*a*	58·4	61·1	2355	5·8	50·9	3·34	0·87	6·99	1·30	2·15	34·48
11*a*	59·0	61·8	2859	4·6	54·0	3·59	1·00	4·85	1·65	1·78	39·08
12*a*	60·1	59·1	3388	3·9	52·6	3·16	0·91	8·93	1·41	1·81	34·18
13*a*	60·2	57·0	3411	3·4	54·5	2·64	0·79	11·50	1·43	1·81	33·69
14*a*	60·0	56·9	3546	3·8	52·5	3·09	0·98	9·83	1·46	1·84	33·07
7*a*	59·6	54·1	3809	5·1	54·7	2·82	0·77	10·90	1·76	1·99	33·70

than with the mineral manure alone. In fact, there is considerably more than twice as much produce, both grain and straw, grown under the influence of ammonium-salts and the mixed mineral manure (7*a*), as with the mixed mineral manure alone (5*a*); and there is one and a half time as much with ammonium-salts and the mixed mineral manure (7*a*), as with ammonium-salts alone (10*a*).

Comparing the different members of the ammonium-salt series one with another, where the ammonium-salts are used alone (10*a*), the produce is much the lowest in amount; with superphosphate added there is more; with superphosphate and either potash, soda, or magnesia, there is more still, but almost identical amounts in the three cases; lastly, with superphosphate and potash, soda, and magnesia together, there is the highest produce among the series.

That there was so little difference in the amount of produce on the three plots, one with soda, one with potash, and one with magnesia, is explained by the fact already recorded, that the plots which received soda, or magnesia, but no potash, in 1852, and each year since, had, before that time, received potash, the effects of the residue of which were very marked for many years, and have only in recent years obviously declined. In reference to this point, it may be stated that Hermann von Liebig, having expressed a wish to examine some of the Rothamsted experimental soils, samples from some of the plots in the experimental wheat field, which had been collected in October, 1865, that is, after the removal of the twenty-second crop from the commencement, and the fourteenth since the application of the same manures year after year on the same plots, were sent to him accordingly. He determined in them the constituents soluble in dilute acetic acid, and the amount of phosphoric acid soluble in dilute nitric acid. The results showed a considerable accumulation of both potash and phosphoric acid where they had been applied in excess; and in each case the accumulation was chiefly in the first 9 inches of depth. Again, Dr. Voelcker's analyses of the drainage-waters from the same field showed comparatively little loss of either potash or phosphoric acid by drainage.

With the very great differences in the amounts of produce grown according to the manure supplied, the Table (X) shows, in the main, corresponding differences in the amounts of nitrogen, total mineral matter, and individual ash-constituents, taken up. For the sake of brevity, attention must chiefly be confined to the variations in the amounts of potash and phosphoric acid in the produce of the different plots.

Of potash, about three times as much was contained in the farmyard manure crop as in the unmanured one; and there was more than three times as much in the crops grown with ammonium-salts and

artificial mineral manure containing potash, as without manure. The quantities of potash in the produce in the other cases when ammonia was applied have an obvious connection with the supply of it. Of the total potash in the crops, only from one-fourth to one-third is accumulated in the grain, excepting in the case of Plot 11*a*, where there is great exhaustion of potash, but otherwise conditions favourable for seed-formation, and here the proportion of the total potash taken up which is accumulated in the grain is greater, and the amount remaining in the straw is proportionally less. On the other hand, the proportion so remaining is the greatest where the supply is the most liberal (2, 13*a*, and 7*a*).

Of phosphoric acid, there is only about twice as much in the highly artificial manured as in the unmanured produce. But a much larger proportion of the whole than in the case of the potash is accumulated in the grain. In fact, whilst only about one-fourth or one-third of the total potash of the crop is accumulated in the grain, about three-fourths, or even more, of the total phosphoric acid of the crop is stored in the grain.

It may be observed in passing, that only a very small proportion (about one-tenth) of the total lime of the crop is found in the seed. Of the total magnesia generally more than one-half, of the sulphuric acid a very small proportion, of the chlorine scarcely a trace, and of the silica the smallest proportion of all, is found in the grain-ash.

Bearing in mind the foregoing facts as to the very variable amounts of the different ash-constituents taken up under the very different conditions as to manuring, and as to the very different distribution of the several constituents in the grain and straw respectively, we are prepared to consider in what proportion they exist to the dry substance of the grain and straw produced, and what is the range of variation in this proportion according to the condition of supply or exhaustion on the different plots. These points are illustrated in Table XI (p. 344).

The general uniformity in the amounts of total ash, nitrogen, and each ash-constituent, in a given quantity of the dry substance of the grain grown under such very varying conditions as to supply, and with such very varying actual amounts taken up by the plant, is very striking. The exceptions to uniformity are so obviously coincident with abnormal exhaustion, or with irregularity in maturation, that the evidence is even the stronger that with equal maturation—that is with uniformity in organic composition—there would be uniformity in mineral composition also. Further, the wide differences in the amounts of the different ash-constituents per 1000 dry matter of the straw show in what variable degrees the constituents have been withdrawn from the general stores of the plant, to provide the necessary

quantities for the all but uniform requirements, for formation or reserve, of a given weight of the final product of the plant—the seed.

Referring to some of the exceptions to uniformity in mineral composition of the grain a little more in detail, it is seen that the lowest proportion of potash is in the grain of Plot 10*a* with ammonium-salts alone, and Plot 11*a* with ammonium-salts and superphosphate (without potash). In these cases, there was very abnormal exhaustion of potash; and consistently with this the proportion of potash in the straw is also very low. It may be noted that with the lower proportion of potash in the dry substance in these cases, there is a somewhat higher proportion of lime in both grain and straw. Again, the uniformity in the proportion of potash in the dry matter of the grain, with ammonium-salts, superphosphate, and soda (with residue of potash 12*a*), with ammonium-salts, superphosphate, and potash (13*a*), with ammonium-salts, superphosphate, and magnesia (with residue of potash 14*a*), with ammonium-salts, superphosphate, soda, potash, and magnesia (7*a*), and with farmyard manure (2), is very marked; whilst the differences in the amounts in the corresponding straws are not only very considerable, but have a very obvious connection with the supply by manure.

The most prominent exceptions to uniformity in the proportion of phosphoric acid in the dry substance of the grain is in the case of Plot 10*a*, with ammonium-salts alone. Here there is very abnormal exhaustion of phosphoric acid, the proportion in the dry substance of the grain is very low, and it is also the lowest in the dry substance of the straw. With the lower proportion of phosphoric acid in the dry substance of the grain in this case, there is the highest proportion of sulphuric acid, but the excess is not at all in equivalent amount.

Thus far it has been sought to elicit the teachings of this second series of wheat grain and straw-ash analyses, by reference to two sets of summary tables; one showing the mean results of the nine plots, for each of the four years, and the other the mean results over the four years, for each of the nine differently manured plots separately. It will be well now to direct attention briefly to the results as given in more detail in the Appendix Tables, X, XI, and XII, in order to ascertain how far such examination leads to accordant conclusions, or brings to view points of interest or importance that would otherwise be overlooked.

The Appendix Table X shows, for each of the nine plots separately, the percentage composition of the ash (of grain and straw) in each of the four years; the first two of which were unfavourable, and the last two favourable for the crop, especially the last of the four. The four seasons were, the first, fifth, seventh, and twelfth, of a series of 12 years. It should be further observed, that after the third of the

four selected years, the supply of potash on the three plots annually receiving it (5*a*, 13*a*, and 7*a*) was reduced to two-thirds the previous amount.

On examination of the table, it is seen that with every condition as to manuring without exception, whether involving an excessive supply or an exhaustion of potash, the percentage of potash in the grain-ash is higher in the two later and better seasons, than in the two earlier but inferior ones. In the straw-ashes again there is, with very different actual percentages in the case of the different plots, uniformly an increase in the percentage of potash in the ash from the first to the third of the four years, and with one exception some decline in the fourth year. The exception is on Plot 7*a*, where, besides ammonium-salts and superphosphate, there is annually applied a considerable excess of potash, soda, and magnesia, salts; but where, as above stated, the amount of potash supplied had then been reduced for several years, notwithstanding which the percentage of potash in the straw-ash is increased. The decline in the percentage of potash in the straw-ash in the fourth and best year of the series in the other cases, is doubtless in great measure explained by the fact, to which attention has already been called, namely, that owing to favourable seed-forming and maturing conditions supervening on great luxuriance, and therefore great accumulation by the plant, its stores were very largely drawn upon in the production of a very unusually large amount of grain.

The details further show that with the uniform increase in the percentage of potash in the grain-ash in the two later and better seasons, there is at any rate a distinct tendency to a reduction in the percentage of magnesia; but not in compensating degree.

Almost equally as marked as the increase in the percentage of potash in the grain-ash, in the later and better years, is the decline in the percentage of phosphoric acid in those years. And as the increase in the percentage of potash in the ash was manifest in the better years even under conditions of exhaustion of it, so here the decline in the percentage of phosphoric acid in the grain-ash in the better years occurs even where there was a liberal annual application of it by manure. The greatest decline is, however, on Plot 10*a*, manured annually with ammonium-salts alone, and where, therefore, there is very abnormal exhaustion of phosphoric acid. Again, with the general decline in the percentage of phosphoric acid in the grain-ash in the later and better years, there is also a general decline in its percentage in the straw-ash in those years, and especially in the last and best year, even where the supply by manure was liberal.

With the general decrease in the percentage of phosphoric acid in both the grain and the straw-ashes in the later years, there is also a

very general, but not uniform increase in the percentage of sulphuric acid. This increase in the percentage of sulphuric acid in the later years is, however, more marked in the straw than in the grain-ashes. Of chlorine, whether the grain itself contained it in any quantity or not, there is scarcely a trace in the grain-ashes. But in the straw-ashes, the percentage is uniformly higher, and sometimes very much higher, in the later and better years. In fact, the increase in the percentage of chlorine in the straw-ashes is more marked than is that of the sulphuric acid.

Whatever may be the case with the sulphuric acid (or its sulphur) there is no evidence leading to the conclusion that chlorine is an essential constituent of the ripened grain; but the question obviously suggests itself, how far the small but variable amounts of sulphuric acid, and the almost total absence of chlorine, in the grain-ashes, have a physiological significance; or whether they are not in a greater or less degree dependent on the conditions of the incineration in the presence of phosphoric acid with less than three of fixed base. Again, there is the question how far the larger and variable amounts of both sulphuric acid and chlorine in the straw-ashes, in a sense compensate the deficiency of phosphoric acid; or how far, having been taken up by the plant, or the sulphuric acid partly due to oxidation of sulphur in the burning, they remain in the ash, containing as it does so little phosphoric acid in proportion to the fixed bases present, though at the same time so much silica. There is in fact a very considerable amount of both sulphuric acid and chlorine in the straw-ashes, notwithstanding the large amount of silica they contain; but it is at the same time to be noted that, as a rule, the relatively high percentages of sulphuric acid and chlorine are in years when the percentage of silica is relatively low.

The influence of the variations in the percentage composition of the ashes on the mineral composition of the dry matter of the produce in the different seasons, is best studied in the Appendix Table XI, in which is shown the amount of each constituent per 1000 of dry matter, grain and straw respectively, in each of the four seasons, under each of the nine different conditions as to manuring.

In discussing the first series of ash-analyses, which related to the produce of three very differently manured plots, in sixteen consecutive seasons, it was seen how small was the variation in the mineral composition of the grain due to manuring, compared with that due to season, that is, to differences in the conditions of seed-formation and maturation. Again, the consideration of the mean results of the nine different conditions as to manuring, in each of the four years (Table VII, p. 336), and of the mean results over the four years, for each of the nine differently manured plots (Table X, pp. 342–343),

showed (10*a* excepted) more variation in the composition of the grain according to season than according to manure.

Quite consistently, the details given in Appendix Table XI, show, under each of the nine conditions as to manuring, a notable difference in the mineral composition of the grain grown in the four different seasons, with their very different seed-forming and maturing conditions, and the very different characters of the grain accordingly. Owing, however, to the different proportions of total ash under these circumstances, and to the generally relatively small amount in the grain of 1863, the differences in the mineral composition of the dry substance of the grain in the different years are by no means so great as might be anticipated from the more marked differences in the percentage composition of the ash itself. Nevertheless, the amount of potash per 1000 dry substance of the grain is, with every condition as to manuring without exception, higher in the favourable season 1858, and almost without exception in the extraordinarily favourable season 1863, than in the two unfavourable seasons. On the other hand, the amount of phosphoric acid per 1000 dry matter, is in 1858 almost without exception, and in 1863 without exception, lower than in the two unfavourable seasons. In the season of 1863, with both very large quantity and very high quality of grain, the proportion of phosphoric acid is indeed very low; and the potash is much lower than in 1858, owing, doubtless, as before explained, to the very favourable seed-forming and maturing tendency, and the consequent great development of organic substance (chiefly starch) in relation to the mineral matter stored up in the grain.

Thus, the results of Series 1, with three very different conditions as to manuring, each over sixteen consecutive seasons, and those of Series 2, relating to nine different conditions as to manuring, each in four very different seasons, consistently show that, under otherwise equal circumstances, the mineral composition of wheat-grain, excepting in cases of very abnormal exhaustion, is very little affected by different conditions as to manuring, provided only that the grain is well and normally ripened. Again, the results consistently show that the composition may vary very greatly with variations of season, that is with variations in the conditions of seed-formation and maturation, upon which the organic composition of the grain depends. In other words, differences in the mineral composition of the ripened grain are associated with differences in its organic composition.

Third Series of Analyses.

In considering the results of the first and second series of ash-analyses, some illustrations of the effects of supply, or exhaustion, have

been given. But as the first series, though relating to the produce of sixteen consecutive seasons, included the results for only three different conditions of manuring, and as the second series, though relating to nine different conditions as to manuring, included results for only four, and those not consecutive seasons, the evidence afforded was in either case somewhat limited. The third series, now to be discussed, was arranged with more special reference to the question of the effects of continuous liberal supply, or of exhaustion, of constituents, both on the quantity and the composition of the produce.

This third series of ash-analyses relates to the produce obtained over a period of twenty consecutive years, 1852—1871 inclusive, on ten differently manured plots, in the experimental wheat field which has now grown the crop every year, commencing 1844, up to the present time. Most of the plots in the field consist of two lands, designated *a* and *b* respectively. Prior to 1852, but especially for the crops of 1846 and 1848, the *a* and the *b* portions were manured somewhat differently, but from 1852 to 1863 inclusive they were manured alike. It will be observed (see p. 331) that in seven out of the nine conditions of manuring to which the second series of analyses relates, the produce was from the *a* portions of the plots; the remaining two not being divided plots. Of the ten plots, the results relating to which are now to be considered, nine are substantially the same as those to which Series 2 relates. Two (2 and 3) are in fact absolutely the same, and the other seven are the duplicate or *b* portions of the plots which, during the whole of the twenty years with which we are now concerned, were manured precisely as described for the *a* portions at p. 331.

The tenth plot now included is 10*b*, which also during the period under consideration, was manured precisely as 10*a*, that is, it receives ammonium-salts alone, and in the same quantities every year. Prior to 1852, however, 10*b* was once (in 1846) unmanured when 10*a* received ammonium-salts; once (1848) 10*b* received a mineral manure comprising potash, soda, magnesia, and superphosphate of lime, as well as ammonium-salts, when 10*a* received ammonium-salts alone; and once (1850) 10*b* received the same mineral manure alone, when 10*a* received ammonium-salts alone. Thus, during the years prior to the period now in question, Plot 10*b* twice received no ammonium-salts when they were supplied to Plot 10*a*, and twice received mineral manure when 10*a* did not. It is of much interest, therefore, to ascertain whether there is any difference of result comparing the one plot with the other, due, on the one hand to less mineral exhaustion on 10*b*, owing to less ammonia having been previously applied, and on the other to mineral manure having been twice directly applied; whether in fact any residue of the mineral manures

twice previously applied remained in the soil, and in a condition available for succeeding crops.

Referring to the footnote at page 331, for details as to quantities, &c., the general description of the manuring of the ten plots is given on the left hand of Table XIII, page 350. The farmyard manure plot, and the unmanured plot, have respectively been under the same treatment every year, from the commencement of the experiments in 1843–4, and each of the other plots from 1851–2.

From the produce of each of the ten plots, ashes were prepared representing the grain and the straw separately, of the ten years 1852–1861, and again of the ten years 1862–1871. It is to be regretted that similar results are not available for a third period of ten years, to 1881 inclusive. The plan adopted was to take, for each of the ten years, an amount of grain proportional to the amount of produce, mix the whole, and prepare the ash from the mixture. For example, supposing the produce in one year were 1000 lbs. of grain per acre, in the next year 1500 lbs., in the next 2000 lbs., and so on, then 1000, 1500, and 2000 parts were taken, and so on, and mixed together. The straw ashes were in like manner prepared from proportional mixtures of the produce of straw.

In the Appendix Table XIII, will be found in detail the percentage composition of the ashes of the grain and straw respectively; in the Appendix Table XIV, the results calculated per 1000 dry matter of the produce (grain and straw); and in Appendix Table XV the results are calculated per acre.

It is obvious that before we can form a trustworthy judgment how far any differences in the composition of the ash, in that of the dry substance of the produce, or in the yield of individual constituents per acre, over the two periods, are due to supply or exhaustion, we must decide whether the first ten or the second ten seasons were the most favourable for the crop, so as to discriminate as far as possible between results due merely to season, and those due to manuring. The following Table, XII, which gives the mean results for the ten plots, over the first and second ten years, as to general characters of the produce, and the yield per acre, of grain, straw, and total produce, of nitrogen, total mineral matter, and of each ash-constituent, will throw light on the characters of the two periods.

It is seen that the second period, though yielding less straw, and less total produce, characters which indicate less luxuriance, that is, less accumulation during the vegetative stages of the development of the plant, nevertheless gives more grain, a higher proportion of grain to straw, and a higher weight per bushel of grain. In fact, whilst in the country at large only three of the first ten years gave more than average produce of grain, six of the second ten gave over average;

TABLE XII.

General Characters of the Produce, and *Quantities per Acre, lbs.* Mean Results for the Ten Plots over each Period.

	Grain.		Straw.		Total produce.	
	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.
Grain to 100 straw	54·5	63·7	—	—	—	—
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Weight per bushel of grain.....	57·1	60·2	—	—	—	—
Produce	1740	1833	3192	2878	4932	4711
Nitrogen.....	29·8	28·0	14·3	11·5	44·1	39·5
Ash (pure)	28·9	28·9	148·7	134·6	177·6	163·5
Lime	0·88	0·98	7·64	8·49	8·52	9·47
Magnesia	3·07	3·10	2·18	2·49	5·25	5·59
Potash	9·47	9·57	29·93	25·35	39·40	34·92
Soda.....	0·06	0·05	0·61	0·83	0·67	0·88
Phosphoric acid	14·68	14·38	4·69	4·28	19·37	18·66
Sulphuric acid .	0·35	0·45	6·47	5·46	6·82	5·91
Chlorine	0·02	0·03	5·23	5·27	5·25	5·30
Silica.....	0·22	0·17	92·26	83·05	92·48	83·22

and whilst the first ten years gave on the whole less than average produce of grain, the second ten gave more than average.

It is clear, therefore, that the first ten years were on the average more favourable for luxuriance, that is, for total accumulation by the plant, but that the second ten were more favourable for seed-formation and maturation.

Accordingly, the table shows that, taking the average of all the plots, there was rather more nitrogen, and more total mineral matter, in the total produce (grain and straw) over the first than over the second ten years; and so far as the individual mineral constituents are concerned, there was, on the average, more potash, phosphoric acid, sulphuric acid, and silica, but less lime, magnesia, soda, and chlorine, taken up and retained in the crops over the first ten years. There was, however, with the more favourable seed-forming tendencies in the second ten years, with the less amount of total mineral constituents taken up by the plant, as much or more of almost every individual mineral constituent accumulated in the grain. The only exception to this of any significance is that there was slightly less phosphoric acid in both grain and straw in the second ten years.

These facts as to the characteristic season effects of the two periods

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on the accumulation of constituents by the plant, and on the distribution of them in grain and straw respectively, must obviously be borne in mind in comparing the results obtained over the two periods on the differently manured plots.

It will be convenient first to examine the evidence of effect of liberal

TABLE XIII.

General Characters of the Produce, and *Quantities per Acre*, on

Plots.	Description of manuring.	Weight per bushel of grain, lbs.		Grain to 100 straw.		Produce per acre, lbs.		
						Grain.		Straw.
		10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.
2.....	Farmyard manure.....	58·8	61·3	56·5	62·7	2145	2385	3795
3.....	Unmanured.....	55·8	59·4	56·8	71·0	944	881	1663
5b	Superphosphate and sulph., pot..sh soda and magn.	57·2	60·5	59·2	67·9	1163	1007	1963
10a	Ammonium salts alone ...	55·1	59·1	52·4	66·3	1318	1553	2516
10b	Ammonium salts alone ...	56·3	59·6	53·2	66·5	1586	1707	2984
11b	Ammonium salts and superphoshate	55·9	58·9	55·5	64·5	1782	1799	3209
12b	Ammonium salts, superphosphate, and soda sulphate	58·0	60·4	54·5	63·3	2101	2173	3857
13b	Ammonium salts, superphosphate, and potash sulphate	58·3	61·2	53·9	59·9	2098	2305	3893
14b	Ammonium salts, superphosphate, and magnesia sulphate.....	58·0	60·6	53·4	64·5	2101	2210	3937
7b	Ammonium salts, superphosphate, and sulph. pot. soda, and magna. ...	57·8	60·7	52·7	59·9	2163	2309	4104
	Direct means	57·1	60·2	54·5	63·7	1740	1833	3192

supply, or exhaustion, of constituents on the different plots, by reference to the difference in the amounts of them taken up and retained per acre, over the two periods; and afterwards to consider the influence of supply or exhaustion as so determined, on the composition of the ash, and on the mineral composition of the dry substance of the produce, grain and straw.

Table XIII records the general characters of the produce of each separate plot, both as to quantity and quality, over each of the ten-year periods.

The Table (XIII) shows that, as when taking the average of the ten plots (Table XII), so under each of the ten different conditions as to manuring, there was a considerably higher proportion of grain to straw, and a considerably higher weight per bushel of the grain, over the second period. On the other hand, in every case (excepting with

farmyard manure, when the quantities were practically equal), there was less produce of straw over the second ten years; and the deficiency is obviously proportionally the greater the more defective the supply by manure. Owing, however, to the much more favourable seed-forming characters over the second period, there is in every case,

TABLE XIII.

each of the Ten Plots, over each of the Two Ten-year Periods.

Produce per acre, lbs.			Nitrogen per acre, lbs.						Plots.
Straw.	Total.		Grain.		Straw.		Total.		
10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	
3803	5940	6188	36·9	36·9	15·9	13·8	52·8	50·7	2
1241	2607	2122	15·6	12·6	7·5	4·9	23·1	17·5	3
1483	3126	2490	19·0	14·5	9·7	5·5	28·7	20·0	5*b*
2341	3834	3894	22·9	25·1	12·3	10·9	35·2	36·0	10*a*
2565	4570	4272	27·5	26·5	14·0	12·1	41·5	38·6	10*b*
2790	4991	4589	31·0	28·1	15·4	13·6	46·4	41·7	11*b*
3431	5958	5604	35·8	33·3	15·8	12·1	51·6	45·4	12*b*
3848	5991	6153	35·1	34·0	15·9	15·5	51·0	49·5	13*b*
3425	6038	5635	36·1	32·8	17·5	13·2	53·6	46·0	14*b*
3857	6267	6166	38·1	36·1	19·2	13·9	57·3	50·0	7*b*
2878	4932	4711	29·8	28·0	14·3	11·5	44·1	39·5	Means.

excepting without manure, and with mineral manure alone—that is, with relative deficiency of available nitrogen—a larger quantity of grain over the later period. In fact, there was more grain over the second period than over the first, wherever there was a liberal supply of ammonium-salts. It was so even where these were applied alone every year of the twenty, and for a greater or less period previously, as on Plots 10*a* and 10*b*, and where therefore there was great mineral exhaustion. Notwithstanding the generally higher produce of grain over the second period, there was, with the less growth of straw, very generally less total produce (grain and straw together) over the second period. The exceptions to this are that, with farmyard manure (2), and with ammonium-salts, superphosphate, and potash, every year (13*b*), there is some little excess over the later years. There is also slight excess, but on a much lower level of actual

produce, even on 10*a*, the most mineral exhausted plot of all, but where there was relatively very full supply of nitrogen by manure.

It is, however, only when we compare plot with plot as to amount of produce that the effects of supply or exhaustion of mineral constituents are clearly indicated. These are best brought out by a comparison of the produce on the plots each of which receives an equal amount of ammonium-salts every year, but under very different conditions as to mineral supply. Thus, with one exception only in the first period, and without exception in the second period, there is marked increase in total produce, the more liberal the supply of phosphoric acid and potash; and there is in each period more than one and a half time as much produce with ammonium-salts, superphosphate, and potash supply (13*b* and 7*b*) as with ammonium-salts alone (10*a*).

Going a little more into detail, there is more produce on 10*b* with ammonium-salts and a residue from previous application of superphosphate and potash, than on 10*a* without such residue; there is more when superphosphate is annually applied afresh (11*b*); there is again more with the further addition of a soda salt (12*b*), or a magnesia salt (Plot 14*b*), with in both cases a considerable residue of potash from previous applications (see p. 345); there is more still with the annual addition of potash (13*b*); and lastly, there is the highest produce in the series on Plot 7*b*, where, besides the ammonium-salts and superphosphate, there is an annual application of potash, soda, and magnesia salts.

Thus there is, with an equal amount of ammonium-salts in each case, a considerable increase by the addition of superphosphate, and a further increase according to the supply of potash. The amounts of produce, therefore, afford clear evidence of the relative exhaustion of available phosphoric acid and potash on some plots, and of the effects of their supply on others. A consideration of the amounts of produce over the second period compared with the first, further illustrates the relative exhaustion of potash on the different plots. Thus on Plots 10*b*, 11*b*, 12*b*, and 14*b*, where there is no annual supply of potash, and the residue from previous applications becomes more and more exhausted, there is notably less produce over the second period; but there is more, or nearly equal produce over the two periods on Plots 13*b* and 7*b*, where the supply of potash is kept up.

The columns showing the average amounts of nitrogen yielded per acre per annum in the produce over the two periods show, with equal amounts supplied by manure, very different amounts taken up and retained on the different plots with their different mineral supplies; there being much more so taken up and retained where there was no deficiency of phosphoric acid or of potash.

We now turn from these general indications of the effects of supply or exhaustion of mineral constituents, to the evidence afforded by the amounts of these in the produce of the different plots, and over the two periods. Table XIV (pp. 358–359) supplies copious illustrations on these points.

Little need be said as to the results relating to Plot 2 with farmyard manure, Plot 3, without manure, and Plot 5*b*, with a complete mineral manure (including phosphoric acid and potash), but without nitrogenous supply. With farmyard manure there is the most, without manure the least, and with the complete mineral manure without nitrogen not much more, total mineral matter stored up in the crop. The details show, however, that the excess of ash-constituents in the crop of the farmyard manure plot is chiefly in silica, but in some degree in phosphoric acid; whilst there is more of every other constituent, potash included, in the produce of one or more of the artificially manured plots.

The most instructive comparison is that between the plots receiving the same amounts of ammonium-salts, with different conditions as to mineral supply by manure. Confining attention first to the amounts of ash-constituents *in the total produce*, it is seen that over the first ten years the quantity increases on the plots in question in the following order: 10*a*, 10*b*, 11*b*, 12*b*, 13*b*, 14*b*, 7*b*, that is, almost exactly in the order of supply by manure, especially of potash. The exception is, that Plot 14*b* without direct potash supply during the period under consideration, but with considerable residue from previous applications, gives, over the first period, slightly more total ash than 13*b* with its annual fresh supply of potash. Over the second period, however, when the residue of potash from previous applications to Plots 12*b* and 14*b* becomes more exhausted, 13*b* with its annual supply yields much more than either. Again, whilst there is considerably less mineral matter taken up over the second period compared with the first on these two plots, there is no reduction in the amount on Plot 13*b* with its constant supply.

There is in fact, whether we compare plot with plot, or period with period, distinct evidence of the influence of supply or exhaustion on the total amount of mineral constituents taken up and retained by the plant.

Referring to the total amounts of individual mineral, or ash-constituents, taken up, the columns relating to potash more clearly indicate the comparative condition of the plots as to the available supply of it. Over the first ten years there was more taken up on 10*b*, with its residue, than on 10*a* without it; there is not quite so much taken up on 11*b*, with superphosphate, as on 10*b*, doubtless owing to greater exhaustion previous to the period under consideration; there is more on Plots 12*b* and 14*b* with their greater previous residue;

and considerably more still on Plots 13*b* and 7*b* with their annual supply. The results relating to the second period illustrate the different condition of the plots still more strikingly. There is, with the increasing exhaustion of it, less potash taken up over the second period than over the first on Plots 10*a*, 10*b*, and 11*b*. But the most instructive comparison is between Plots 12*b*, 13*b*, and 14*b*. On

TABLE XIV.

Average Amounts, *per Acre per Annum*, in lbs., of Total Mineral Matter (Pure of each Plot, over each of

Plots.	Ash (pure).		Ferric oxide.		Lime.		Magnesia.		Potash.	
	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.
					Grain.					
2	37·1	38·5	0·20	0·18	0·93	1·00	4·05	4·23	11·8	12·4
3	16·4	14·9	0·12	0·09	0·51	0·48	1·72	1·56	5·5	4·9
5*b*	20·4	17·3	0·13	0·09	0·54	0·49	2·15	1·84	6·6	5·7
10*a*	20·8	22·7	0·16	0·14	0·81	0·99	2·17	2·47	7·1	7·7
10*b*	25·1	25·5	0·17	0·15	0·85	1·06	2·65	2·77	8·5	8·7
11*b*	29·3	27·4	0·18	0·13	1·13	1·18	3·09	2·90	9·3	8·8
12*b*	34·7	34·0	0·19	0·18	1·03	1·22	3·67	3·61	11·4	11·4
13*b*	34·4	36·3	0·23	0·22	0·99	1·07	3·62	3·83	11·3	12·2
14*b*	34·7	35·0	0·25	0·19	1·00	1·20	3·71	3·83	11·3	11·8
7*b*	36·2	36·9	0·26	0·21	1·01	1·09	3·84	3·96	11·9	12·3
Mean	28·9	28·9	0·19	0·16	0·88	0·98	3·07	3·10	9·5	9·6
					Straw.					
2	205·4	209·5	0·91	0·60	8·14	8·90	2·59	3·03	40·8	41·1
3	84·8	70·0	0·62	0·45	4·27	3·58	1·27	1·09	13·5	10·4
5*b*	106·4	86·2	0·79	0·57	4·26	3·62	1·34	1·24	20·0	15·4
10*a*	111·5	108·1	0·71	0·45	6·62	8·00	1·81	2·19	20·2	15·4
10*b*	127·7	110·2	1·07	0·47	7·56	8·84	2·11	2·47	24·8	16·3
11*b*	146·0	122·5	0·84	0·56	8·68	10·49	2·36	2·78	21·6	17·2
12*b*	169·4	153·7	0·88	0·60	8·95	11·17	2·48	2·97	34·0	26·4
13*b*	173·6	172·1	0·86	0·55	9·07	10·18	2·41	2·86	41·9	43·0
14*b*	175·6	148·3	0·85	0·60	9·25	10·24	2·73	3·24	38·5	27·5
7*b*	186·5	165·3	1·04	0·56	9·62	9·92	2·71	3·03	44·1	40·7
Mean	148·7	134·6	0·86	0·54	7·64	8·49	2·18	2·49	29·9	25·3
					Total Produce.					
2	242·5	248·0	1·11	0·78	9·07	9·90	6·64	7·26	52·6	53·5
3	101·2	84·9	0·74	0·54	4·78	4·06	2·99	2·65	19·0	15·3
5*b*	126·8	103·5	0·92	0·66	4·80	4·11	3·49	3·08	26·6	21·1
10*a*	132·3	130·8	0·87	0·59	7·43	8·99	3·98	4·66	27·3	23·1
10*b*	152·8	135·7	1·24	0·62	8·41	9·90	4·76	5·24	33·3	25·0
11*b*	175·3	149·9	1·02	0·69	9·81	11·67	5·45	5·68	30·9	26·0
12*b*	204·1	187·7	1·07	0·78	9·98	12·39	6·15	6·58	45·4	37·8
13*b*	208·0	208·4	1·09	0·77	10·06	11·25	6·03	6·69	53·2	55·2
14*b*	210·3	183·3	1·10	0·79	10·25	11·44	6·44	7·07	49·8	39·1
7*b*	222·7	202·2	1·30	0·77	10·63	11·01	6·55	6·99	56·0	53·0
Mean	177·6	163·5	1·05	0·70	8·52	9·47	5·25	5·59	39·4	34·9

Plots 12*b* and 14*b*, with their rapidly reducing available residue of potash from previous applications, there is a great reduction in the amount taken up over the second period compared with the first, whereas on Plot 13*b*, with its liberal annual supply, there is even more taken up over the second period, though it was one of less general luxuriance. There is in fact over the first period about twice,

TABLE XIV.

Ash), and of each Ash-Constituent, in the Grain, Straw, and Total Produce, the Two Ten-year Periods.

Soda.		Phosphoric acid.		Sulphuric acid.		Chlorine.		Silica.		Plots.
10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	
Grain.										
0·08	0·06	19·6	20·1	0·20	0·34	trace	0·01	0·3	0·2	2
0·04	0·02	8·2	7·5	0·23	0·22	trace	0·01	0·1	0·1	3
0·05	0·02	10·5	8·8	0·17	0·30	trace	trace	0·2	0·1	5*b*
0·04	0·05	9·6	10·4	0·59	0·69	0·12	0·10	0·2	0·1	10*a*
0·06	0·04	12·2	12·0	0·42	0·58	0·04	0·07	0·2	0·2	10*b*
0·03	0·07	14·9	13·6	0·46	0·53	trace	0·05	0·2	0·2	11*b*
0·07	0·07	17·7	17·0	0·47	0·40	trace	trace	0·2	0·2	12*b*
0·04	0·05	17·7	18·2	0·25	0·52	trace	trace	0·2	0·2	13*b*
0·06	0·04	17·9	17·6	0·26	0·35	trace	trace	0·2	0·2	14*b*
0·08	0·04	18·4	18·5	0·42	0·54	trace	trace	0·2	0·2	7*b*
0·06	0·05	14·7	14·4	0·35	0·45	0·02	0·03	0·2	0·2	Mean.
Straw.										
0·23	0·32	6·9	7·2	6·99	6·14	6·78	7·25	133·6	136·6	2
0·27	0·14	2·6	2·2	3·48	2·50	1·71	1·57	57·5	48·5	3
0·15	0·18	4·2	3·5	4·59	4·05	2·59	2·12	69·1	56·0	5*b*
0·95	0·91	3·4	3·0	5·62	5·26	3·20	2·69	69·7	70·8	10*a*
0·74	1·21	3·8	2·8	5·85	4·84	4·06	3·63	78·7	70·4	10*b*
1·54	2·40	4·9	4·4	6·34	5·67	3·59	4·60	96·9	75·3	11*b*
0·90	1·70	5·5	4·8	7·54	6·26	6·05	5·74	104·4	95·3	12*b*
0·36	0·11	5·2	5·1	7·89	6·68	8·27	9·81	99·6	96·0	13*b*
0·56	1·07	5·0	4·8	8·08	6·17	7·54	6·00	104·8	90·0	14*b*
0·42	0·27	5·4	4·9	8·35	7·07	8·52	9·33	108·3	91·6	7*b*
0·61	0·83	4·7	4·3	6·47	5·46	5·23	5·27	92·3	83·0	Mean.
Total Produce.										
0·31	0·38	26·5	27·3	7·19	6·48	6·78	7·26	133·9	136·8	2
0·31	0·16	10·8	9·7	3·71	2·72	1·71	1·58	57·6	48·6	3
0·20	0·20	14·7	12·3	4·76	4·35	2·59	2·12	69·3	56·1	5*b*
0·99	0·96	13·0	13·4	6·21	5·95	3·32	2·79	69·9	70·9	10*a*
0·80	1·25	16·0	14·8	6·27	5·42	4·10	3·70	78·9	70·6	10*b*
1·57	2·47	19·8	18·0	6·80	6·20	3·59	4·65	97·1	75·5	11*b*
0·97	1·77	23·2	21·8	8·01	6·66	6·05	5·74	104·6	95·5	12*b*
0·40	0·16	22·9	23·3	8·14	7·20	8·27	9·81	99·8	96·2	13*b*
0·62	1·11	22·9	22·4	8·34	6·52	7·54	6·00	105·0	90·2	14*b*
0·50	0·31	23·8	23·4	8·77	7·61	8·52	9·33	108·5	91·8	7*b*
0·67	0·88	19·4	18·7	6·82	5·91	5·25	5·30	92·5	83·2	Mean.

and over the second period with the declining amount where it was not applied, about two and a half times as much potash accumulated in the total crop (grain and straw), where it was liberally supplied as where it was the most exhausted (10*a*), the supply of nitrogen being equal in the two cases.

It may be noted that throughout the ammonium-salt series there is rather more of both lime and magnesia taken up over the second period than the first; and the excess, especially of lime, is generally the greater where there is the more evidence of exhaustion of potash.

Comparing plot with plot in the ammonium-salt series, the amount of phosphoric acid taken up, though obviously not independent of supply by manure, varies considerably with equal supply of it; and the variations, especially over the second period, are obviously in some degree connected with the potash supply, and the variations in growth dependent thereon.

Further examination of the Table (XIV) will show that, comparing plot with plot, the amounts of potash accumulated in the grain show a less, and those remaining in the straw a greater range of variation, according to supply, than do the total amounts accumulated in the crop. In other words, by the exigencies of grain-formation, the stores of the entire plant have yielded up to the grain a much larger proportion of the total amount taken up in some cases than in others. For example, over the first period the amounts of potash in the total produce of plots 12*b*, 13*b*, and 14*b*, are respectively, 45·4, 53·2, and 49·8 lbs. per acre, whilst the amounts in the grain are 11·4, 11·3, and 11·3 lbs., and those remaining in the straw are 34·0, 41·9, and 38·5 lbs. Over the second period, the point is still more clearly illustrated. Thus, the amounts of potash in the total produce of the three plots were: 37·8, 55·2, and 39·1 lbs.; the amounts in the grain were 11·4, 12·2, and 11·6 lbs., and in the straw they were 26·4, 43·0, and 27·5 lbs. It is obvious that the amounts taken up on 13*b*, with the annual supply, were in excess of those required for the grain-formation of the seasons in question.

Upon the whole, the evidence is quite distinct that the amounts of mineral constituents found in the total crop on the different plots were very directly influenced by their supply or exhaustion within the soil. It is also clear that, even under equal conditions as to supply of nitrogen, characters of season, and other circumstances, the final distribution of the mineral constituents in the grain and straw respectively is not in proportion to the amount in the total plant, but is materially influenced by the seed-forming characteristics of the seasons; the amount accumulated in the grain being fairly equal with very different amounts stored in the total plant, provided this supply be not below a certain limit.

It is then established, that the amounts of the mineral or ash-constituents found in the total crop, have a very direct connection with the amounts available within the soil; but that the amounts stored up in the grain are little influenced by the quantity taken up, provided this is not deficient. It is in fact proved that the conditions of the experiments were such as to supply the data necessary for the elucidation of the questions with a view to the solution of which they were selected, and the analyses executed. We are now prepared to consider the influence of supply, or exhaustion, on the percentage composition of the ash, of the grain, and of the straw, and on the relation of the mineral constituents to the dry substance of the produce.

Table XV (pp. 362–363) shows the percentage of nitrogen, and of total mineral matter (pure ash), in the dry substance of the grain, and of the straw, of each plot, over each of the two periods. It also shows the percentage composition of the ash in each case.

Attention has already been called to the facts that, taking the mean of all the plots, there was a lower percentage of total mineral matter in the dry substance of the grain over the second period with its higher seed-forming, and better maturing characters; and that, with the lower proportion of total ash in the grain of the better quality, there was nevertheless a somewhat higher percentage of potash and lime, a lower percentage of phosphoric acid and silica, and with this a higher percentage of sulphuric acid, in the ash.

Turning to the potash columns in Table XV, the details show a higher percentage in the ash over the second period than over the first, under each of the very different conditions as to manure, with the single exception of the unmanured plot (3). It is also seen within what comparatively narrow limits the percentage of potash in the grain-ash varies under such very widely different conditions as to supply of it within the soil. Its percentage in the straw-ashes, on the other hand, varies very much more. Thus, in the grain-ashes the percentage of potash varies in the first period from 31·7 to 34·0, and in the second period, with its better maturing conditions, from 32·1 to 34·1; whilst in the corresponding straw-ashes it varies in the first period from 14·8 to 24·1, and in the second period from 14·1 to 25·0.

Although the percentage of potash in the grain-ashes is thus comparatively uniform, the variations, comparing plot with plot, are nevertheless consistent with the variations in the conditions of the different plots. Thus, comparing the results for the four plots each with ammonium-salts and superphosphate, one with soda (12*b*), one with potash (13*b*), one with magnesia (14*b*), and one with potash, soda, and magnesia (7*b*), in addition, the percentages of potash in the grain-ashes are, over the first period, 32·8, 32·9, 32·6, and 32·9; that

Table XV.

Percentage of Nitrogen, and Total Mineral Matter (Pure Ash), in the Dry Sub-
the Percentage of each Con-

Plots.	Nitrogen.		Ash (pure).		Ferric oxide.		Lime.		Magnesia.		Potash.
	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–61.	10 years, 1862–'71.	10 years, 1852–'61.
					Grain.						
2.....	2·05	1·84	2·06	1·92	0·53	0·45	2·49	2·59	10·9	11·0	31·7
3.....	1·98	1·70	2·08	2·00	0·72	0·57	3·13	3·22	10·4	10·5	33·5
5*b* ...	1·95	1·71	2·10	2·03	0·63	0·52	2·66	2·82	10·5	10·7	32·3
10*a* ...	2·07	1·90	1·88	1·72	0·73	0·61	3·90	4·35	10·4	10·9	34·0
10*b* ...	2·07	1·82	1·88	1·75	0·67	0·56	3·41	4·17	10·6	10·9	33·9
11*b* ...	2·07	1·84	1·96	1·79	0·61	0·46	3·87	4·31	10·5	10·6	31·7
12*b* ...	2·03	1·80	1·97	1·84	0·56	0·52	2·97	3·57	10·6	10·6	32·8
13*b* ...	1·99	1·74	1·95	1·86	0·66	0·62	2·88	2·96	10·5	10·5	32·9
14*b* ...	2·05	1·75	1·97	1·87	0·72	0·53	2·87	3·41	10·7	11·0	32·6
7*b* ...	2·09	1·85	1·99	1·89	0·71	0·56	2·79	2·94	10·6	10·7	32·9
Mean	2·04	1·80	1·98	1·86	0·65	0·54	3·10	3·43	10·6	10·7	32·8
					Straw.						
2.....	0·50	0·43	6·44	6·55	0·45	0·29	3·96	4·25	1·27	1·45	19·9
3.....	0·54	0·47	6·08	6·68	0·73	0·65	5·03	5·12	1·49	1·56	15·9
5*b* ...	0·59	0·44	6·45	6·91	0·74	0·66	4·00	4·20	1·26	1·44	18·8
10*a* ...	0·58	0·55	5·27	5·46	0·64	0·42	5·93	7·41	1·63	2·02	18·2
10*b* ...	0·56	0·56	5·11	5·08	0·84	0·43	5·92	8·02	1·65	2·24	19·4
11*b* ...	0·57	0·58	5·41	5·24	0·58	0·46	5·94	8·56	1·63	2·26	14·8
12*b* ...	0·49	0·42	5·25	5·32	0·52	0·39	5·29	7·27	1·46	1·93	20·1
13*b* ...	0·49	0·48	5·35	5·32	0·50	0·32	5·22	5·91	1·38	1·66	24·1
14*b* ...	0·53	0·46	5·31	5·15	0·48	0·41	5·27	6·90	1·55	2·18	22·0
7*b* ...	0·56	0·43	5·43	5·11	0·56	0·34	5·15	6·00	1·46	1·83	23·7
Mean	0·53	0·48	5·56	5·56	0·60	0·44	5·17	6·36	1·48	1·86	19·7

is very nearly identical, but slightly higher on the two plots receiving potash (13*b* and 7*b*). Further, in the second period, the percentages in the grain-ashes of the same four plots are: 33·3, 33·5, 33·1, and 33·4, again almost identical, but with a tendency to higher results on the two plots having an annual supply. The corresponding straw-ashes, on the other hand, show very wide differences, which have a very marked connection with the known differences as to supply. Thus, the percentages of potash in the straw-ashes of the four plots are, over the first period, 20·1, 24·1, 22·0, and 23·7; and over the second period, with the increasing exhaustion on the first and third plots, 12*b* and 14*b*, they are, 17·2, 25·0, 18·5, and 24·6.

The differences in the percentages of potash in the other grain-ashes are also consistent and significant. The lowest percentages in the grain-ashes are in those of 11*b*, 2, and 5*b*. In the case of 11*b*, with

TABLE XV.

stance of the Grain and Straw of each Plot, over each of the Two Periods; also *stituent in the Pure Ash.*

Potash.	Soda.		Phosphoric acid.		Sulphuric acid.		Chlorine.		Silica.		Plots.
10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	
					Grain.						
32·2	0·22	0·16	52·8	52·2	0·55	0·89	0·01	0·02	0·77	0·56	2
33·2	0·23	0·13	49·8	50·3	1·40	1·44	0·03	0·07	0·71	0·60	3
32·8	0·26	0·10	51·7	50·9	0·82	1·69	0·01	0·02	1·00	0·59	5*b*
34·1	0·18	0·22	46·3	45·8	2·84	3·03	0·59	0·42	1·17	0·66	10*a*
34·1	0·23	0·17	48·6	47·0	1·69	2·26	0·16	0·27	0·78	0·60	10*b*
32·1	0·11	0·26	50·8	49·7	1·56	1·91	0 01	0·18	0·83	0·56	11*b*
33·3	0·19	0·20	51·0	50·0	1·37	1·18	0·01	0·01	0·60	0·57	12*b*
33·5	0·14	0·14	51·5	50·2	0·71	1·43	0·01	0·01	0·71	0·60	13*b*
33·1	0·18	0·10	51·6	50·3	0·73	1·00	0·01	0·01	0·67	0·64	14*b*
33·4	0·20	0·12	51·0	50·1	1·16	1·46	0·01	0·01	0·69	0·64	7*b*
33·2	0·19	0·16	50·5	49·6	1·28	1·63	0·09	0·10	0·79	0·60	Mean.
					Straw.						
19·6	0·11	0·15	3·34	3·43	3·40	2·93	3·30	3·46	65·1	65·2	2
14·8	0·32	0·21	3·09	3·11	4·11	3·57	2·01	2·25	67·8	69·2	3
17·9	0·14	0·21	3·93	4·12	4·32	4·70	2·43	2·46	65·0	64·9	5*b*
14·2	0·85	0·84	3·05	2·79	5·05	4·86	2·87	2·49	62·5	65·5	10*a*
14·8	0·58	1·09	2·97	2·55	4·58	4·40	3·18	3·30	61·6	63·9	10*b*
14·1	1·06	1·96	3·39	3·63	4·35	4·63	2·45	3·75	66·4	61·5	11*b*
17·2	0·53	1·11	3·24	3·14	4·46	4·07	3·58	3·73	61·7	62·0	12*b*
25·0	0·21	0·06	2·98	2·97	4·55	3·89	4·75	5·69	57·4	55·8	13*b*
18·5	0·32	0·73	2·85	3·24	4·60	4·16	4·29	4·05	59·7	60·7	14*b*
24·6	0·23	0·16	2·90	2·98	4·48	4·28	4 56	5·64	58·0	55·4	7*b*
18·1	0·44	0·65	3·17	3·20	4·39	4·15	3·34	3·68	62·5	62·4	Mean.

ammonium-salts and superphosphate, there is forced luxuriance to the utmost limits attainable with the conditions of great exhaustion of potash, which latter is clearly indicated by the very low percentage in the straw-ashes. In the case of Plot 2, with farmyard manure, the low percentages in the grain-ashes are not due to deficient supply, as corroborated by the comparatively high amounts in the straw-ashes; but rather to a full supply of every constituent throughout the periods of growth and maturation, and a different character of ripening accordingly, as indicated by very high phosphoric acid, and very low sulphuric acid. That the percentage is also low in the grain-ashes of Plot 5*b*, with full mineral supply, including potash, but no nitrogen supplied, is doubtless dependent on the total want of luxuriance during the earlier stages, and to eventual sluggish ripening. Lastly, the highest percentages of all are in the grain-ashes of Plots 10*a* and 10*b*, with ammonium-salts alone, giving forced luxuri-

ance as far as the mineral supply will permit, but where there is known great exhaustion of both potash and phosphoric acid, and so far as can be judged, greater of phosphoric acid than of potash; especially in the second period, as indicated by the low percentages in the straw-ashes. These conditions of mineral exhaustion must obviously materially affect the characters of the maturation.

It is at least noteworthy that, with the generally higher percentages of potash in the grain-ashes of the second period with its more favourable seasons, there is also in the case of every plot a higher percentage of lime, and a slight tendency to higher percentage of magnesia over that period. A study of the details further shows, comparing plot with plot, that the percentages of lime are generally the higher where the exhaustion of potash is known to be the greatest, as, for instance, in the grain-ashes of Plots 10*a*, 10*b*, and 11*b*; and again in those of Plots 12*b* and 14*b*, compared with those of 13*b* and 7*b*.

Turning to the phosphoric acid columns, it is seen that there is as distinct a tendency to lower percentages in the grain-ashes of the later and better seasons, as there was to higher percentages of potash over those seasons. This is very marked in the case of the four comparable Plots 12*b*, 13*b*, 14*b*, and 7*b*. The influence of relative exhaustion of phosphoric acid, that is exhaustion having regard to the amount of crop grown, is also very clear. Thus, both the actual and relative exhaustion of phosphoric acid is undoubtedly the greatest on Plots 10*a* and 10*b*, and it is in the grain-ashes of these plots that we have the lowest percentages of phosphoric acid in the first period, and lower still, and again the lowest over the second period.

With the generally lower percentages of phosphoric acid in the grain-ashes in the second ten years, there is in every case (excepting 12*b*) a higher percentage of sulphuric acid; and comparing plot with plot the percentage of sulphuric acid is, over both periods, the highest where the exhaustion, and the percentage, of phosphoric acid are the lowest (10*a* and 10*b*). Again, with the generally lower percentages of phosphoric acid in the grain-ashes over the second period, there is, under every condition as to manuring, a lower percentage of both ferric oxide and silica; and small as are the actual percentages of these constituents in the grain-ashes, the result is too uniform to be without some significance.*

* With regard to both ferric oxide and silica it should be stated, however, that their relative amounts in ashes are very generally found to rise and fall with the amounts of "sand," and as the amounts of this are liable to be higher in the less favourably matured and harvested crops, we should expect less ferric oxide and silica due to adventitious matters in the more favourable seasons. It may be added that the mean percentages of sand in the grain-ashes were, in those of Series 1, 1·66, of Series 2, 0·99, and of Series 3, 0·91; and in the straw-ashes they were, in those of

It may perhaps be considered established that iron plays an important part during the vegetative or green stages of the life of the plant; but there is not evidence of equal weight leading to the conclusion that iron is essential to grain formation; though its accumulation in the seed may be of importance when the young plant grown from it first produces green leaves.

We now turn from a consideration of the percentage composition of the ashes, to that of the relation of the mineral constituents to the organic substance produced. This is shown in Table XVI (pp. 366–367).

It is seen that, with a lower proportion of total ash-constituents in the second and better maturing period, there is (with slight exceptions in the case of the lime and the sulphuric acid), a lower proportion of each individual ash-constituent in the dry substance of the grain under each of the very different conditions as to manuring. This lower proportion of ash-constituents to organic substance produced, is moreover coincident with a lower proportion of nitrogen in the dry substance, under each of the ten conditions as to manuring. It is also coincident with a higher weight per bushel of the grain in every case. The lower proportion of the several ash-constituents is therefore associated with better ripening, a lower proportion of nitrogenous, and a higher proportion of non-nitrogenous, constituents (carbohydrates), produced.

To go a little more into detail:—

It will be remembered that the grain-ashes showed (with one exception) a higher percentage of potash under every condition as to manuring over the second and more favourable period than over the first; but when the potash is calculated, not to 100 of ash, but to 1000 of dry substance, we find with the lower proportion of total mineral matter, a lower proportion of potash in the dry substance of the grain of the later and better maturing period, under every condition of manuring without exception. And whereas there was the apparent anomaly of relatively high percentage of potash in the grain-ash where it was much exhausted (10*a* and 10*b*), we have the lowest proportion to the dry substance produced on the three most potash-exhausted plots (10*a*, 10*b*, and 11*b*), namely, 6·39, 6·39, and 6·22, in the first period, and 5·87, 5·98, and 5·76, over the second period, with its greater exhaustion. The straws of these plots also show the lowest proportion of potash to dry substance.

Again, on the four comparable plots, 12*b*, 13*b*, 14*b*, and 7*b*, the quantities of potash *per* 1000 *dry substance of grain*, are, over the first

Series 1, 2·23, of Series 2, 2·19, and of Series 3, 2·28. Comparing the results for the two periods of Series 3, the mean percentage of sand in the grain-ashes of the first period was 1·09, and of the second period, 0·73; and in the straw-ashes it was, in those of the first period 2·74, and of the second period 1·81.

TABLE XVI.

Quantity of Mineral Matter (pure Ash), and of each Ash-

Plots.	Ash (pure).		Ferric oxide.		Lime.		Magnesia.		Potash.	
	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.
Grain.										
2	20·6	19·2	0·11	0·09	0·51	0·50	2·25	2·10	6·52	6·18
3	20·8	20·0	0·15	0·11	0·65	0·65	2·17	2·11	6·98	6·65
5*b*	21·0	20·3	0·13	0·11	0·56	0·57	2·21	2·16	6·79	6·66
10*a*	18·8	17·2	0·14	0·11	0·73	0·75	1·96	1·88	6·39	5·87
10*b*	18·8	17·5	0·13	0·10	0·64	0·73	1·99	1·90	6·39	5·98
11*b*	19·6	17·9	0·12	0·08	0·76	0·77	2·06	1·90	6·22	5·76
12*b*	19·7	18·4	0·11	0·09	0·58	0·66	2·08	1·95	6·46	6·14
13*b*	19·5	18·6	0·13	0·11	0·56	0·55	2·05	1·96	6·43	6·22
14*b*	19·7	18·7	0·14	0·10	0·56	0·64	2·11	2·04	6·41	6·16
7*b*	19·9	18·9	0·14	0·11	0·55	0·56	2·11	2·03	6·53	6·33
Mean	19·8	18·6	0·13	0·10	0·60	0·63	2·10	2·00	6·48	6·16
Straw.										
2	64·4	65·5	0·29	0·19	2·55	2·78	0·81	0·95	12·80	12·83
3	60·8	66·8	0·44	0·43	3·06	3·42	0·91	1·04	9·65	9·91
5*b*	64·5	69·1	0·48	0·45	2·58	2·90	0·81	0·99	12·09	12·34
10*a*	52·7	54·6	0·34	0·23	3·13	4·04	0·86	1·10	9·57	7·76
10*b*	51·1	50·8	0·43	0·22	3·02	4·08	0·84	1·14	9·90	7·53
11*b*	54·1	52·4	0·31	0·24	3·22	4·48	0·88	1·18	8·00	7·37
12*b*	52·5	53·2	0·27	0·21	2·78	3·86	0·77	1·03	10·54	9·14
13*b*	53·5	53·2	0·26	0·17	2·80	3·15	0·74	0·88	12·90	13·29
14*b*	53·1	51·5	0·26	0·21	2·80	3·56	0·82	1·13	11·65	9·55
7*b*	54·3	51·1	0·30	0·17	2·80	3·06	0·79	0·94	12·84	12·58
Mean	55·6	55·6	0·32	0·22	2·86	3·50	0·81	1·03	11·19	10·46

period, 6·46, 6·43, 6·41, and 6·53, or almost identical amounts; and over the second period, 6·14, 6·22, 6·16, and 6·33, that is, lower amounts, and quantities which are nearly, but not quite, as uniform as those over the first period. The differences, slight as they are, are, however, quite consistent with the known differences as to available supply. Thus, the residue from previous applications of potash to plots 12*b* and 14*b* was becoming much reduced, and the accumulations from annual supply to plots 13*b* and 7*b* were becoming greater over the second period; and accordingly there is a slightly lower proportion of potash in the dry substance of the grain of the two potash exhausted plots; and the proportions in the dry substance of the straw of the four plots show very wide differences, due to supply on the one hand, and to exhaustion on the other. Thus, on the two potash exhausted plots, 12*b* and 14*b*, the proportions of potash in the dry substance of the straw are 9·14 and 9·55, and on the two plots with annual supply they are 13·29 and 12·58.

Table XVI.

Constituent *per* 1000 *Dry Substance of Grain and of Straw.*

Soda.		Phosphoric acid.		Sulphuric acid.		Chlorine.		Silica.		Plots.
10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	
Grain.										
0·05	0·03	10·87	10·01	0·11	0·17	trace	trace	0·16	0·11	2
0·05	0·03	10·37	10·07	0·29	0·29	trace	0·01	0·15	0·12	3
0·06	0·02	10·86	10·35	0·17	0·35	trace	0·01	0·21	0·12	5*b*
0·03	0·04	8·70	7·89	0·53	0·52	0·11	0·07	0·22	0·11	10*a*
0·04	0·03	9·16	8·24	0·32	0·39	0·03	0·05	0·15	0·11	10*b*
0·02	0·05	9·95	8·92	0·31	0·34	trace	0·03	0·16	0·10	11*b*
0·04	0·04	10·05	9·21	0·27	0·22	trace	trace	0·12	0·10	12*b*
0·03	0·03	10·05	9·31	0·14	0·27	trace	trace	0·14	0·11	13*b*
0·04	0·02	10·15	9·38	0·15	0·19	trace	trace	0·13	0·12	14*b*
0·04	0·02	10·12	9·49	0·23	0·28	trace	trace	0·14	0·12	7*b*
0·04	0·03	10·05	9·25	0·24	0·29	0·01	0·02	0·15	0·11	Mean.
Straw.										
0·07	0·10	2·15	2·25	2·19	1·92	2·13	2·27	41·91	42·71	2
0·19	0·14	1·88	2·08	2·49	2·39	1·22	1·50	41·19	46·25	3
0·09	0·14	2·53	2·84	2·78	3·25	1·57	1·70	41·88	44·83	5*b*
0·45	0·46	1·61	1·52	2·66	2·66	1·51	1·36	32·94	35·75	10*a*
0·30	0·56	1·52	1·29	2·34	2·23	1·62	1·67	31·47	32·47	10*b*
0·57	1·03	1·84	1·90	2·35	2·42	1·33	1·97	35·94	32·20	11*b*
0·28	0·59	1·70	1·66	2·34	2·17	1·88	1·99	32·39	32·96	12*b*
0·11	0·03	1·59	1·58	2·43	2·06	2·55	3·03	30·70	29·66	13*b*
0·17	0·37	1·51	1·67	2·45	2·14	2·28	2·09	31·69	31·28	14*b*
0·12	0·08	1·57	1·52	2·43	2·19	2·48	2·88	31·50	28·29	7*b*
0·23	0·34	1·75	1·77	2·42	2·25	1·95	2·17	34·48	34·28	Mean.

The percentages of phosphoric acid in the grain-ashes varied more according to supply or exhaustion than did those of the potash, but with one exception (the unmanured plot 3), the percentage was lower over the second period than the first. In every case, without exception, Table XVI shows a lower proportion of phosphoric acid in the dry substance of the grain over the second period; and over both periods a much wider range of variation in the proportion comparing plot with plot, that is, according to supply or exhaustion, than in the case of the potash. Thus, in the first period the proportion of phosphoric acid in 1000 dry substance of the grain ranged from 8·70 with ammonium-salts alone, to 10·87 with farmyard manure; and in the second period from 7·89 with ammonium-salts alone to 10·35 with mineral manure alone. On the other hand, the four plots, 12*b*, 13*b*, 14*b*, and 7*b*, show almost uniform proportions, namely, 10·05, 10·05, 10·15, 10·12, over the first period, and 9·21, 9·31, 9·38, and 9·49, over the second period. The very low proportions of phosphoric acid in

the dry substance of the grain under the conditions of very abnormal exhaustion of it on Plots 10*a* and 10*b*, with ammonium-salts alone, are accompanied, over the first period with very low weight per bushel of the grain, indicating low condition of maturation, and over the second period with lower weights per bushel than on the four plots above referred to. There is also very low proportion of phosphoric acid in the dry substance of the grain of Plot 11*b* with an annual application of superphosphate, and therefore relative excess of phosphoric acid supplied, but with nevertheless very defective grain formation owing to great exhaustion of potash; and here again there is very low weight per bushel. As indicated in the percentage composition of the ash, there is also in proportion to the dry substance, the highest amount of sulphuric acid with the lowest amounts of phosphoric acid in the grain of Plots 10*a* and 10*b*, but by no means in compensating equivalent proportion.

The results of this third series of ash-analyses, specially arranged to trace the effects of supply or exhaustion of ash-constituents on the composition of the ash, and of the crop, agree with those of Series 1 and 2, in showing, in the case of the grain, much greater uniformity in the composition of the ash, and in the proportion of ash-constituents to dry substance, than in that of the straw. It is seen that, under otherwise equal conditions, the amounts of the mineral constituents taken up by the plant over a given area, depend very directly on the amounts in available condition within the soil. Further, with very different amounts so taken up over a given area, the amounts stored up in the grain will, other conditions being equal, be very nearly uniform; whilst the amounts remaining in the straw will have a very obvious connection with the supply or exhaustion.

The results also agree with those of the former series, in showing very distinctly the influence of season on the composition of the grain-ashes, and on the proportion of the ash-constituents to the dry substance of the grain; and that these differences in the mineral composition of the grain, dependent on season, are associated with very different conditions as to maturation, and accordingly with different characters of the organic substance produced.

As, however, this third series of ashes represents the average produce of two periods, respectively of ten years each, which, though of obviously varying average characters, do not show anything like the extremes of individual good and bad seasons, the results do not illustrate in so marked a manner the varying effects of season as do those of Series 1 and Series 2. On the other hand, the analytical results last considered do represent very marked variations in the conditions of supply, or exhaustion, of mineral constituents. Hence, contrary to those before discussed, they show a wider range in the mineral

composition according to manure than according to season. Nevertheless, it is evident that, when the supply of any mineral constituent is not defective below a certain limit in relation to the other conditions of growth, the mineral composition of the grain is very uniform. It is, indeed, very uniform, notwithstanding there may be a very great excess of supply, and a relatively very great excess taken up by the plant, in which latter case a large excess remains in the straw. In fact, the composition of the grain only varies in any marked degree according to manure, when there is very abnormal deficiency of one or more constituents, having regard to the amount of growth which is induced by the liberal supply of others.

At the commencement of our paper, it was stated that it was not proposed to treat the subject exhaustively. Accordingly, attention has mainly been confined to an attempt to point out some of the most important conclusions to which a consideration of the enormous amount of experimental result recorded, seemed to lead. The discussion has nevertheless necessarily been one of much detail. It has at the same time served to raise many points of interest, and to suggest lines of study which neither the time nor the space at our disposal will allow us to follow up. There are, indeed, various aspects of the subject, chemical, physiological, and agricultural, which it might be expected we should consider. Some of these will be more appropriately discussed when the results of the analyses of the ashes of other crops than wheat have been given. Thus, we have a series of ash-analyses relating to the produce of barley grown under different conditions as to season and manuring; a series relating to some leguminous crops, including the bean-plant at different stages of growth; a series relating to root-crops, and to potatoes; a series relating to crops grown in rotation, but with different manures; and lastly, a large series relating to the mixed herbage of grass land, that is to the mixed produce of numerous species of plants growing in association, which are not allowed fully to ripen, but are cut at various stages of development short of complete maturation. In the meantime we submit the results relating to the mineral composition of wheat-grain and wheat-straw, with such comments as their study seemed to suggest, as a substantial contribution to a limited branch of the subject of the ash-constituents of our crops.

In conclusion, extensive and comprehensive as has been the inquiry within its own limits, it must be borne in mind that the results relate to the produce obtained on one description of soil, and in one locality only.* Still, the number of very widely different seasons

* It is true that once within the period to which the results relate, there was a change of seed from one description to another not very widely different; but there

over which the experiments have extended, and the very widely different conditions as to manuring of the different plots, have probably provided a much greater range of conditions of growth than would have been secured had the experiments been made in fewer seasons, on various soils, and in various localities, but with more normal conditions as to manuring. Indeed, the conditions of relative excess, or exhaustion, of the available supply of individual constituents represented in the experiments the results of which have been recorded, are probably much more distinctive and characteristic than could be obtained under more normal conditions. On this view it is obvious that, whilst the results are of a very marked character, and are therefore very instructive if properly interpreted, it must not be without careful reservation that their application to the circumstances of actual agricultural practice should be inferred.

Summary and Conclusions.

The investigation comprises the analyses of 92 wheat-grain and 92 wheat-straw ashes, and, including 69 duplicates, the number of complete ash-analyses involved is 253. Every ash is of produce of known history of growth as to soil, season, and manuring; all the specimens having been grown in the experimental field at Rothamsted which has now yielded wheat for forty years in succession, 1844 to 1883 inclusive. The results are arranged in three Series.

First Series of Analyses.

1. This series includes results obtained under three very characteristically different conditions as to manuring, in each case for sixteen consecutive seasons. The manuring conditions were:—Plot 2, farmyard manure every year; that is, with an excessive supply both of nitrogen, and of mineral, or ash-constituents. Plot 3, without manure every year; that is, with exhaustion of both nitrogen and ash-constituents. Plot 10*a*, with ammonium-salts alone every year; that is, with an excess of supplied nitrogen, but with great relative deficiency of ash-constituents. The results thus illustrate the influence of fluctuations of season from year to year, under known but very different conditions as to manuring.

2. There was a much greater range of variation in the percentages of potash and phosphoric acid in the ashes, both of grain and straw, due to variations of season, than to variations of manure. The range

is no evidence leading to the conclusion that this irregularity has at all vitiated the comparative character of the results, or the legitimacy of the conclusions that have been drawn from them.

of variation due to season, was much the greater in the straw-ashes; which is explained by the fact that favourable or unfavourable seed-forming and ripening may supervene on conditions of high or of low luxuriance, that is, of great or of limited activity of accumulation of constituents by the plant; hence the withdrawal of constituents for seed-formation will leave very various amounts of migratory matters in the straw.

3. Taking high weight per bushel of the grain as a fairly good indication of high quality, and *vice versâ*, there was, with each condition of manuring, a general and marked, but not uniform tendency to low proportions of nitrogen, of total mineral constituents (ash), and of individual ash-constituents, in the dry substance of the grain of the seasons of higher quality. That is, the higher quality of the grain is associated with the greater accumulation of the non-nitrogenous matters (carbohydrates) in proportion to the nitrogen, and to the mineral constituents which have been stored up.

4. *Per* 1000 *dry substance of the grain* there is, with each condition as to manuring, much greater uniformity in the amount, and a rather lower average amount of potash in the eight better than in the eight worse seasons. Yet, it is in a very unfavourable season that there was actually the lowest, and in the worst season of the sixteen that there was actually the highest, proportion of potash in the dry substance of the grain; that is, the very different results are obtained under defective, but very different, conditions of development and maturation.

5. *Per* 1000 *dry substance of the grain* there is, under each of the three conditions as to manuring, a lower average amount of phosphoric acid over the eight better seasons, and it is lower in individual seasons of high quality. Still there is a wider range than among the eight inferior seasons, and wider than in the case of the potash. In the case of the farmyard manure plot, the lower proportion of phosphoric acid in the better seasons cannot be due to exhaustion, but to enhanced production of organic substance. The average proportion of phosphoric acid to organic substance is, however, lower without manure than with farmyard manure, and lower still with ammonium-salts alone, in which case there is very abnormal mineral exhaustion.

6. The details illustrate in a striking manner the greater influence of season than of manuring on the proportion of the ash-constituents to the organic substance of the grain. With normal maturation it is, under otherwise comparable conditions, nearly uniform with different conditions as to manuring; and deviations from normal mineral composition are associated with deviations from normal development of the organic substance.

7. The percentage of silica in the dry substance of the straw is

lower in the seasons of more favourable maturation. In fact, stiffness of straw depends on favourable development of the woody substance, by the increase of which the proportion of the accumulated silica to the organic substance is reduced.

8. Excluding the ferric oxide and the silica, and calculating the whole of the phosphoric acid as tribasic, the grain-ashes show more than one and a half time as much acid as base; and even calculating the whole of the phosphoric acid, whether combined with alkalis or earths, as bibasic, there is still an excess of acid. The straw-ashes, calculated in the same way, show a considerable excess of base, even reckoning the whole of the phosphoric acid as tribasic; but they contain more than 60 per cent. of silica. The question arises whether carbonic acid (if any), and some sulphuric acid and chlorine, have not been expelled in the incineration; in the case of the grain-ashes in the presence of acid-phosphates, and in that of the straw-ashes in the presence of an excess of silica.

9. Investigations at Rothamsted and elsewhere have established that there is a general increase in the percentage of nitrogen proceeding from the finer to the coarser flours obtained from the same wheat-grain, and that there is marked increase in the more branny portions, the greatest concentration being immediately below the pericarp. The percentage of potash, lime, magnesia, and phosphoric acid, also increases from the finer to the coarser flours, and it is the highest in the branny products. The percentage of potash is about ten times, of lime four or five times, of magnesia fifteen to twenty times, and of phosphoric acid more than ten times, as high in the dry substance of the bran as in that of the finer flours. It is also established that, in comparable cases, the better matured grains contain the lower percentages of nitrogen and total mineral matter, and a higher percentage of starch; and the ash-analyses now under consideration consistently show a lower proportion of the chief individual mineral constituents in the grains of better quality.

10. The average annual amounts of total mineral constituents in the crops *per acre* (grain and straw) over the sixteen years were—with farmyard manure 237·4 lbs., without manure 106·1 lbs., and with ammonium-salts alone 142 lbs.; that is, with ammonium-salts one and a third time, and with farmyard manure more than twice, as much as without manure. With ammonium-salts, the greatest proportional increase was in lime, potash, magnesia, soda, sulphuric acid, and chlorine, and the least in phosphoric acid. With farmyard manure, by far the greatest increase was in potash, of which there is more than two and a half times as much as without manure; and there is about twice as much magnesia, and more than twice as much lime, phosphoric acid, sulphuric acid, soda, and silica, and nearly four times as much chlorine.

11. Comparing the amounts of the individual ash-constituents *in the crops per acre* over the first eight years with those over the second eight, they are, without manure, in the grain nearly identical; but in the straw there is more or less deficiency of every constituent, excepting lime, over the second period. Deficiency in the straw and total produce generally, but not uniformly, indicates deficient source. With farmyard manure, there was more of every ash-constituent (excepting sulphuric acid), in the grain, straw, and total produce, over the second period; the most marked increase being, in the grain in potash and phosphoric acid, and in the straw in potash and silica. With ammonium-salts alone there was, over the second period, in the grain slight deficiency of potash and magnesia, and greater in phosphoric acid, but there was slight increase in lime and sulphuric acid. In the straw there was more marked deficiency in every constituent, excepting sulphuric acid, and the deficiency is the most marked in potash, phosphoric acid, chlorine, and silica, though chlorine is largely supplied in the ammonium-salts.

12. Upon the whole, the comparison of the yield of ash-constituents *per acre* over the first and second eight years shows—without manure a small relative exhaustion of both potash and phosphoric acid, and with ammonium-salts a greater relative exhaustion of both.

13. *Per* 1000 *dry substance of grain* there were, taking the average of the sixteen years, almost identical amounts of each of the ash-constituents without manure, and with farmyard manure; but with ammonium-salts alone there was marked deficiency, especially of phosphoric acid, and in a less degree of potash. *Per* 1000 *dry substance of straw*, there was, without manure considerably less potash than with farmyard manure, but otherwise not much difference. With ammonium-salts alone, there was still greater deficiency of potash, but more lime, less phosphoric acid, but more sulphuric acid, and considerably less silica, than either without manure or with farmyard manure.

14. Comparing the amounts of ash-constituents *per* 1000 *dry substance of the grain, over the first and second eight years*, with farmyard manure they are almost identical over the two periods, and without manure very nearly so, but there is slightly less potash, and more magnesia and phosphoric acid, over the second period—conditions indicating less perfect maturation, that is, less flour in proportion to bran. With ammonium-salts alone, the dry substance of the grain shows a marked deficiency of potash and magnesia, and especially of phosphoric acid, compared with that of the other plots; it nevertheless shows very little difference comparing the second eight years with the first, though there is a slight decrease of phosphoric acid, and increase of sulphuric acid and silica, over the second period.

15. *Per* 1000 *dry substance of the straw*, the amount of the various ash-constituents varies more over the two periods than in the case of the grain, but still comparatively little. Without manure there is, over the second period, a deficiency of potash and magnesia, partially compensated by lime, also a deficiency of phosphoric acid. With ammonium-salts, the most marked deficiency over the second period is of potash; there is also less chlorine, but more sulphuric acid.

16. In conclusion, in regard to this first series of ash-analyses, although the results show a much wider range of variation in the mineral composition of the grain due to season than to manuring, there are still distinct differences due to the very different conditions as to manuring; but with each of the three conditions there is comparatively little difference over the first and the second eight years. With ammonium-salts alone, where there is very abnormal mineral exhaustion, the dry substance of the grain shows relative deficiency of both potash and phosphoric acid, but especially the latter. Upon the whole, the results point to great uniformity in the mineral composition of the grain under the different conditions of manuring, provided only that it is perfectly and normally ripened. High or low percentage of nitrogen is also more dependent on the conditions of maturation than on full or limited supply of it by the soil.

Second Series of Analyses.

1. This series relates to the produce obtained under nine different conditions as to manuring, each in two unfavourable, and in two favourable seasons for the crop. They thus illustrate the influence of characteristic seasons under a great variety of manuring conditions.

2. The manuring conditions were:—Farmyard manure; without manure; superphosphate, and sodium, potassium, and magnesium sulphates; ammonium-salts alone; ammonium-salts and superphosphate; ammonium-salts, superphosphate, and sodium sulphate; ammonium-salts, superphosphate, and potassium sulphate; ammonium-salts, superphosphate, and magnesium sulphate; ammonium-salts, superphosphate, and sodium, potassium, and magnesium sulphates.

3. The four seasons were:—1852 and 1856, which were unfavourable, and 1858 and 1863, which were favourable for the crop. 1852 (the ninth from the commencement of the experiments) was bad both as to quantity and quality of produce. 1856 gave fairly average quantity, both of grain and straw, but the crop was unevenly ripened, and the quality of the grain was low. 1858 yielded only a moderate amount of total produce, but more than average proportion and amount of grain, which was of over average quality. 1863 (the

twentieth year of the experiments) was the best both as to quantity and quality of produce throughout the forty years, 1844–1883, inclusive.

4. Taking the mean results of the nine plots in each of the four seasons, there was from the first to the fourth season an increase in the weight per bushel of the grain, and in the proportion of grain to straw, and a decrease in the percentages of nitrogen and total mineral matter in the dry substance of the grain. Coincidently with these characters, there was, from the first to the fourth season, great increase in the percentage of potash, and considerable decrease in that of magnesia, and there was great decrease in the percentage of phosphoric acid, and an increase in that of sulphuric acid, *in the grain-ash.*

5. *Calculated per* 1000 *dry substance of the grain*, there was more potash, and less magnesia, and especially much less phosphoric acid, and some more sulphuric acid, in the produce of the two later and better seasons. These are indications of higher proportion of flour to bran, that is, of more starch. The variation in the mineral composition is thus associated with variation in the organic composition of the grain. *Per* 1000 *dry substance of the straw*, there was also more potash, less phosphoric acid, and more sulphuric acid, in the better seasons.

6. *Calculated per acre*, there was about twice as much grain, nearly one and a half time as much straw, and more than one and a half time as much total produce, in the best as in the worst of the four seasons. Of total nitrogen *in the crops per acre*, there was an average of only 38 lbs. in 1852, and of 50·1 lbs. in 1863; whilst of the less total quantity in 1852 a considerably larger actual amount remained in the straw. In 1852, 61·6 per cent., in 1856, 72·9 per cent., in 1858, 73·8 per cent., and in 1863, 77·4 per cent., of the total nitrogen of the crops was stored up in the grain. In 1863, with the largest actual amount of nitrogen in the grain *per acre*, there was the lowest *percentage of it in the grain;* that is, under the influence of the very favourable growing and maturing conditions, there was a greater accumulation of non-nitrogenous constituents in proportion to the amount of nitrogen stored up.

7. *Calculated per acre*, there was, in 1863, one and a third time as much total mineral matter in the crop as in either of the other years. Comparing the best and the worst seasons (1863 and 1852), there was one and a half time as much lime, magnesia, and phosphoric acid, and about twice as much potash and sulphuric acid, in the total produce *per acre*, in the season of most favourable growth and maturation. Yet, *per* 1000 *dry substance of the grain*, the amounts of lime, magnesia, and phosphoric acid were lower, and the amount of potash was not much higher, in the better seasons.

8. Taking the average results over the four years, for each of the nine different conditions as to manuring separately, there is, with one or two exceptions, comparatively little variation in weight per bushel with the equal season, but very varying manuring conditions; and the differences, such as they are, are consistent. The percentage of nitrogen is also in the main fairly uniform with the different manures; but it is low with mineral manure alone and great nitrogen exhaustion, and high with ammonium-salts alone and relatively excessive nitrogen supply. The percentages of total mineral matter are also fairly uniform; but somewhat high with farmyard manure, without manure, and with mineral manure alone, and low with ammonium-salts alone.

9. *Per* 1000 *dry substance of the grain*, there is also general uniformity in the amount of the chief individual ash-constituents under the very different manuring conditions. The exceptions to uniformity in the amounts of potash are, that it is somewhat high without manure and with purely mineral manure, and somewhat low with ammonium-salts alone, and with ammonium-salts and superphosphate, but without potash. The exceptions to general uniformity in the amounts of phosphoric acid are, that it is high with farmyard manure, without manure, and with purely mineral manure, and low with ammonium-salts alone.

10. *Per* 1000 *dry substance of the straw*, the amounts of the individual ash-constituents are much more variable on the different plots. The variation is especially marked in the case of the potash and phosphoric acid, and it is obviously much dependent on their supply. It is also very marked in the case of the silica.

11. *Calculated per acre*, there is very great variation in the amounts of produce, and of its various constituents, according to manure. Without manure, and with purely mineral manure, the produce was very small; it was much more with ammonium-salts alone, and much more still with ammonium-salts and mineral manure together. With ammonium-salts and the most complete mineral manure, there was more than one and a half time as much total produce as with ammonium-salts alone, and nearly two and a half times as much as with mineral manure alone. There were in the main corresponding differences in the amounts of nitrogen, total mineral matter, and the chief individual ash-constituents, stored up in the crops.

12. Of potash, the ashes show three times as much in the total produce *per acre* with farmyard manure, and more than three times as much in that with ammonium-salts and mineral manure containing potash, as without manure. On the other plots (excepting with mineral manure alone), the quantities of potash in the crops are obviously dependent on the supply. Of the total potash of the crops,

there is generally only from one-fourth to one-third accumulated in the grain.

13. Of phosphoric acid, there was little more than twice as much *per acre* in the highly manured as in the unmanured produce; but three-fourths or more of the total phosphoric acid of the crop may be accumulated in the grain.

14. Of the total lime and sulhuric acid of the crop, a very small proportion, of the magnesia generally more than half, of the chlorine scarcely a trace, and of the silica the smallest proportion of all, is found in the grain-ashes.

15. With very great variation in the amounts of nitrogen and ash-constituents *in the total crop per acre* on the different plots, there is remarkable uniformity in the amounts of each *per* 1000 *dry substance of grain;* but wide variation in the amounts *per* 1000 *dry substance of straw.* The greatest exceptions to uniformity in the amount of potash per 1000 dry substance of the grain are, that it is low with ammonium-salts alone, or with superphosphate only in addition (10*a* and 11*a*), and high without manure, and with purely mineral manure (3 and 5*a*). The most marked deviations from general uniformity in the amount of phosphoric acid in the dry substance of the grain are, that it is low with ammonium-salts alone (10*a*), and high with farmyard manure, without manure, and with purely mineral manure (2, 3, and 5*a*).

16. With every condition of manuring there is, *in the grain ashes*, a higher percentage of potash, and lower of phosphoric acid, and somewhat lower of magnesia also, in the two favourable seasons, indicating higher proportion of flour to bran. There is lower percentage of phosphoric acid in the better seasons even where there is liberal supply of it, but the lowest is on Plot 10*a*, where it is the most exhausted. The *straw-ashes* also show a higher percentage of potash in the two better seasons.

17. With decline in the percentage of phosphoric acid in the ashes, there is increase in sulphuric acid; and in the straw-ashes increase of chlorine in a greater degree. It is a question how far the small amounts of sulphuric acid and chlorine in the grain-ashes are due to the presence of so much acid-phosphate; and how far the much larger amounts in the straw-ashes are due to their excess of base to acid, other than silica, although of this there is so much.

18. *Calculated per* 1000 *dry substance of the grain*, there is, with every condition as to manuring, a higher amount of potash in 1858, and almost without exception in 1863, than in the two unfavourable seasons. On the other hand, the proportion of phosphoric acid is in 1858 almost without exception, and in 1863 without exception, lower than in the unfavourable seasons.

19. The second series of analyses, as did the first, consistently show considerable variation in the mineral composition of wheat-grain, according to season, but little according to manuring (excepting in cases of abnormal exhaustion), provided the seed be properly matured. In fact, variations in the mineral composition are associated with differences in the organic composition.

Third Series of Analyses.

1. This series was more specially arranged to trace the influence of supply or exhaustion. The ashes represent the produce obtained under ten different conditions as to manuring, each over ten years, 1852–1861, and ten years, 1862–1871. Nine of the plots are substantially duplicates of those to which Series 2 relates; and the tenth, 10*b*, is a duplicate of 10*a*, with ammonium-salts alone, excepting that twice prior to the period now under consideration it received mineral manure, including potash and phosphoric acid, when 10*a* did not.

2. The average results *per acre*, of the ten plots, for each of the two periods, show that the first ten years were on the average the more favourable for luxuriance, that is, for total accumulation by the plant, and the second ten the more favourable for seed-formation and maturation. Accordingly, with less mineral matter in the total produce per acre over the second ten years, there was as much or more of almost every individual ash-constituent accumulated in the grain.

3. With each condition of manuring where the nitrogen supply was not deficient, there was more grain, and of better quality, over the second ten years. Comparing plot with plot, there was, over both periods, with equal nitrogen supply, considerable increase by the addition of superphosphate and potash. Comparing the second period with the first, the influence of supply, or exhaustion, especially of potash, is very marked (10*a*, 10*b*, 11*b*, 12*b*, 14*b*, 13*b*, and 7*b*).

4. With equal supply of nitrogen, very variable amounts of it are found in the total produce per acre of the different plots, according to the associated mineral supply.

5. Of individual ash-constituents there was more in the *total produce per acre* with some of the artificial manures than with farmyard manure. Comparing the plots with equal ammonium-salts but different potash supply, the amounts of potash in the total produce are in the order of the supply.

6. Comparing Plots 12*b*, 13*b*, 14*b*, and 7*b*, all with the same nitrogen supply, but the first and third with a decreasing residue of potash from previous applications, and the second and fourth with an annual supply of it, the amounts of potash in the *total produce per acre per*

annum over the first ten years are—45·4, 53·2, 49·8, and 56·0, but the amounts in the grain are 11·4, 11·3, 11·3, and 11·9; over the second period, with the further exhaustion on the first and third plots (12*b* and 14*b*), the amounts of potash in the total produce are 37·8, 55·2, 39·1, and 53·0, but the amounts accumulated in the grain are 11·4, 12·2, 11·6, and 12·3. Thus, the amounts in the total produce are directly influenced by the supply or exhaustion, especially over the second period; but over each period the amounts in the grain are nearly identical on the four plots, showing only slight relative deficiency over the second period on Plots 12*b* and 14*b*, with their reducing residue of potash supply.

7. The amount of phosphoric acid in the *total produce per acre* varies much with equal supply of it, and of nitrogen, and is obviously much dependent on the available supply of potash. The amounts of mineral constituents accumulated in the total plant (as indicated by the amounts in the total crop) are very directly influenced by the supply or exhaustion; but, other things being equal, the final distribution in the grain is influenced much more by the seed-forming characters of the season than by the amounts of the constituents in the total plant, provided there be not a deficiency.

8. *Percentage Composition of the Ashes.*—As in the case of the mean results for the ten plots, so in that of each plot (excepting plot 3, without manure), there is a higher percentage of potash in the grain-ashes of the second period with its better seed-forming and maturing tendencies. The percentage of potash in the grain-ashes only varies from 31·7 to 34·0 over the first, and from 32·1 to 34·1 over the second period; but in the straw-ashes it varies from 14·8 to 24·1 over the first, and from 14·1 to 25·0 over the second period. The variations in the straw-ashes are consistent with the variations in the supply.

9. Comparing Plots 12*b*, 13*b*, 14*b*, and 7*b*, the percentages of potash in the grain-ashes are—over the first period 32·8, 32·9, 32·6, and 32·9, and over the second period 33·3, 33·5, 33·1, and 33·4; but in the straw-ashes they are—over the first period 20·1, 24·1, 22·0, and 23·7, and over the second period, with the increasing exhaustion on the first and third plots (12*b* and 14*b*), 17·2, 25·0, 18·5, 24·6.

10. With higher percentages of potash in the grain-ashes over the second period, there are also higher percentages of lime, and there is a tendency to higher percentages of magnesia; but there is in every case, excepting without manure, a lower percentage of phosphoric acid, and with this, in every case but one, a higher percentage of sulphuric acid, over the second period.

11. *Per* 1000 *dry substance of the grain* there is generally a lower amount of each ash-constituent (excepting lime and sulphuric acid)

over the later and better seed-forming and maturing period; there is also a lower amount of nitrogen, and therefore a higher proportion of non-nitrogenous constituents. Comparing plot with plot, the amounts of potash *per* 1000 *dry substance of the grain* are fairly uniform; but even in the grain, and in the straw in a much more marked degree, it is lowest where it is the most exhausted. Comparing Plots 12*b*, 13*b*, 14*b*, and 7*b*, the amounts *per* 1000 *dry substance of the grain* are—over the first period 6·46, 6·43, 6·41, and 6·53, and over the second period 6·14, 6·22, 6·16, and 6·33; but in the straw they are—over the first period 10·54, 12·90, 11·65, and 12·84, and over the second period, with the increasing exhaustion on the first and third plots, 9·14, 13·29, 9·55, and 12·58.

12. The amounts of phosphoric acid *per* 1000 *dry substance of the grain* varied more according to supply than did that of the potash; but it was, with every condition of manuring, lower over the second and more favourable period. Over the first period, it ranged from 8·70 to 10·87, and over the second from 7·89 to 10·35. On Plots 12*b*, 13*b*, 14*b*, and 7*b* it was—over the first period 10·05, 10·05, 10·15, and 10·12, and over the second period 9·21, 9·31, 9·38, and 9·49, or much lower over the second period, but within each period almost uniform on the four plots. Taking the whole series of plots, it was the lowest on 10*a* and 10*b*, where it was most exhausted, but it was also low on 11*b*, where it was annually supplied, though without potash, and with defective development accordingly.

13. The results of the third series of analyses agree with those of the first and second in showing, upon the whole, marked uniformity in the mineral composition of the ripened grain, even when there is wide variation in that of the straw dependent on supply or exhaustion. They also show distinct influence of season, and that the differences in the mineral composition of the grain due to season are associated with differences in the organic composition. With less variation in the conditions of season, and of influence therefrom, but with a wider range of mineral supply, or exhaustion, than in the other series, there is a wider range in the mineral composition of the grain according to supply or exhaustion; it is, however, comparatively little influenced by excess of supply, but more by deficiency. The three series show that, under otherwise comparable conditions, there is, in the better matured grain, that is in the grain of higher quality, a lower percentage of total mineral matter (ash); *in the ash*, a higher percentage of potash, but lower of phosphoric acid; but *in the dry substance of the grain*, generally a lower percentage of potash, and considerably lower of phosphoric acid, and also a lower percentage of nitrogen.

APPENDIX-TABLES,

I—XV.

Composition of the Ash of Wheat-Grain, and of Wheat-

Appendix-Table I.—General Characters of the Produce, and *Percentage Com-*
Straw, in sixteen consecutive

Plot 2.—Farmyard Manure, every year.

Harvests	1848	1849	1850	1851	1852	1853	1854	1855
Grain to 100 straw	56·0	68·3	57·3	66·2	49·6	33·2	60·1	58·2
Weight per bushel of grain, lbs.	58·2	63·8	61·9	63·6	58·2	51·1	62·5	62·0
Composition of the Grain, per cent.								
Dry matter	79·68	82·76	83·92	84·50	83·25	80·27	85·88	83·68
Nitrogen } in dry matter	1·89	1·58	1·86	1·57	2·02	1·76	1·70	2·19
Ash (pure) } in dry matter	2·03	1·93	2·04	1·93	1·98	2·20	1·98	2·08
Composition of the Grain-Ash (pure), per cent.								
Ferric oxide	1·23	0·78	1·15	0·88	0·95	0·83	0·62	0·70
Lime	2·41	2·52	2·80	2·88	2·79	2·60	2·46	2·49
Magnesia	10·81	10·55	11·07	11·11	12·77	10·15	11·27	11·04
Potash	30·15	33·07	31·35	32·36	27·22	35·46	31·97	30·91
Soda	0·57	0·68	0·81	0·50	0·45	0·54	0·48	0·84
Phosphoric anhydride	52·66	50·33	50·48	50·69	54·69	47·05	52·21	53·29
Sulphuric anhydride	0·55	1·51	1·42	0·92	0·14	2·35	0·47	0·03
Chlorine	0·08	0·03	none	trace	trace	0·11	0·02	none
Silica	1·56	0·53	0·92	0·66	0·99	0·93	0·50	0·70
Total	100·02	100·00	100·00	100·00	100·00	100·02	100·00	100·00
Deduct O = Cl	0·02	—	—	—	—	0·02	—	—
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Composition of the Straw, per cent.								
Dry matter	81·46	82·46	82·50	85·42	82·16	80·66	84·89	84·00
Nitrogen } in dry matter	0·49	0·45	0·50	0·48	0·46	0·73	0·35	0·43
Ash (pure) } in dry matter	6·49	6·64	6·27	6·66	7·04	6·64	4·90	7·40
Composition of the Straw-Ash (pure), per cent.								
Ferric oxide	0·59	0·78	0·61	0·44	0·85	0·44	0·33	0·28
Lime	4·00	5·09	5·21	4·20	3·87	3·22	5·31	3·57
Magnesia	1·27	1·76	2·14	1·87	1·52	1·36	1·96	1·30
Potash	15·73	17·19	19·05	17·72	12·86	20·14	19·66	21·01
Soda	0·28	0·55	0·94	0·54	0·60	0·52	0·46	0·45
Phosphoric anhydride	4·52	2·98	4·26	4·60	3·21	6·21	3·04	3·89
Sulphuric anhydride	2·92	4·27	3·62	3·34	2·58	3·55	4·62	2·36
Chlorine	2·05	2·93	3·80	2·77	1·86	2·68	3·24	5·02
Silica	69·10	66·11	61·23	65·15	73·07	62·48	62·11	63·23
Total	100·46	100·66	100·86	100·63	100·42	100·60	100·73	101·11
Deduct O = Cl	0·46	0·66	0·86	0·63	0·42	0·60	0·73	1·11
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

Straw, grown at Rothamsted, year after year on the same Land.

position of the Ash (excluding Sand and Charcoal), of the Grain, and of the Seasons, 1848–1863.

Plot 2.—Farmyard Manure, every year.

1856	1857	1858	1859	1860	1861	1862	1863	Average.	Harvests.
52·8	77·9	65·5	47·1	54·2	71·0	58·3	67·5	58·6	Grain to 100 straw.
58·6	60·4	62·6	56·5	55·5	60·5	61·0	63·1	60·0	Wt. per bushel of grain, lbs.
									Composition of the Grain, per cent.
82·58	85·63	83·56	82·70	85·50	84·65	83·27	84·63	83·75	Dry matter.
1·89	1·97	1·91	2·09	2·00	1·95	1·57	1·52	1·83	Nitrogen } in dry matter.
1·98	1·94	2·04	2·11	2·15	2·15	1·99	1·85	2·01	Ash (pure) } in dry matter.
									Composition of the Grain-Ash (pure), per cent.
0·86	1·05	0·90	0·78	1·02	0·49	0·76	0·43	0·84	Ferric oxide.
2·53	2·88	2·61	2·37	2·78	2·52	2·51	2·34	2·59	Lime.
11·71	11·97	11·17	11·18	10·13	10·29	11·12	11·41	11·11	Magnesia.
29·27	29·84	31·87	31·18	33·78	33·13	32·00	31·54	31·57	Potash.
0·42	0·77	0·28	0·54	0·65	0·65	0·66	0·66	0·59	Soda.
54·18	52·53	51·88	52·64	49·44	51·41	51·61	52·04	51·70	Phosphoric anhydride.
0·23	0·46	0·75	0·51	0·87	1·01	0·51	0·93	0·79	Sulphuric anhydride.
0·07	0·01	0·06	trace	0·07	none	none	trace	0·03	Chlorine.
0·75	0·49	0·49	0·80	1·28	0·50	0·83	0·65	0·79	Silica.
100·02	100·00	100·01	100·00	100·02	100·00	100·00	100·00	100·01	Total.
0·02	—	0·01	—	0·02	—	—	—	0·01	Deduct O = Cl.
100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	Total.
									Composition of the Straw, per cent.
83·08	84·42	85·24	84·68	85·00	85·83	83·88	84·44	83·81	Dry matter.
0·38	0·39	0·47	0·40	0·56	0·43	0·37	0·25	0·44	Nitrogen } in dry matter.
6·57	5·45	6·42	6·24	7·91	7·17	6·69	6·42	6·52	Ash (pure) } in dry matter.
									Composition of the Straw-Ash (pure), per cent.
0·49	0·80	0·44	0·61	0·84	0·23	0·39	0·18	0·52	Ferric oxide.
3·98	5·46	4·03	4·56	3·20	3·39	3·23	3·78	4·13	Lime.
1·57	1·61	1·69	1·34	1·06	1·20	1·34	1·41	1·52	Magnesia.
14·62	20·11	21·70	18·62	16·70	25·62	14·53	17·97	18·33	Potash.
0·53	0·44	0·49	0·54	0·51	0·71	0·54	none	0·51	Soda.
3·42	3·46	3·41	3·52	4·04	3·62	3·28	3·16	3·79	Phosphoric anhydride.
2·62	2·67	3·57	2·04	2·54	3·50	2·29	2·54	3·00	Sulphuric anhydride.
2·29	4·01	4·81	2·78	1·95	4·98	1·84	3·61	3·16	Chlorine.
71·00	62·31	60·95	66·62	69·60	57·87	72·98	68·16	65·75	Silica.
100·52	100·87	101·09	100·63	100·44	101·12	100·42	100·81	100·71	Total.
0·52	0·87	1·09	0·63	0·44	1·12	0·42	0·81	0·71	Deduct O = Cl.
100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	Total.

Composition of the Ash of Wheat-Grain, and of Wheat-

Appendix-Table II.—General Characters of the Produce, and *Percentage* of the Straw, in sixteen con-

Plot 3.—Unmanured, every year.

Harvests	1848	1849	1850	1851	1852	1853	1854	1855
Grain to 100 straw	55·6	76·1	58·2	66·6	53·9	25·4	63·6	60·0
Weight per bushel of grain, lbs.	57·3	61·4	60·6	61·1	56·6	45·9	60·6	59·2
Composition of the Grain, per cent.								
Dry matter	80·34	82·28	83·80	84·30	82·57	80·12	84·67	84·76
Nitrogen } in dry matter	2·17	1·73	1·83	1·67	2·08	2·09	1·92	2·14
Ash (pure) } in dry matter	2·00	1·88	2·02	1·94	2·03	2·36	1·95	2·02
Composition of the Grain-Ash, per cent.								
Ferric oxide	1·37	1·07	1·32	0·72	1·07	1·26	0·60	0·61
Lime	2·87	3·15	2·98	2·98	2·87	3·09	2·67	2·64
Magnesia	10·35	9·72	9·86	10·16	11·67	10·27	10·44	9·93
Potash	31·19	35·34	32·97	34·74	29·66	35·49	34·18	33·92
Soda	0·66	0·42	0·91	0·45	0·61	0·54	0·73	0·49
Phosphoric anhydride	51·41	47·71	49·68	49·07	51·79	45·55	49·35	50·79
Sulphuric anhydride	0·79	1·83	1·14	1·13	0·99	2·40	1·56	0·65
Chlorine	0·02	0·02	0·04	0·03	0·04	0·19	0·02	0·06
Silica	1·34	0·74	1·11	0·72	1·31	1·25	0·45	0·92
Total	100·00	100·00	100·01	100·00	100·01	100·04	100·00	100·01
Deduct O = Cl	—	—	0·01	—	0·01	0·04	—	0·01
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Composition of the Straw, per cent.								
Dry matter	81·00	82·08	82·64	84·28	82·84	81·59	83·30	82·77
Nitrogen } in dry matter	0·53	0·49	0·53	0·57	0·57	0·85	0·39	0·48
Ash (pure) } in dry matter	6·77	7·02	7·03	6·54	7·04	6·27	5·16	7·30
Composition of the Straw-Ash, per cent.								
Ferric oxide	1·12	1·01	0·47	0·78	1·03	0·94	0·49	0·48
Lime	2·78	2·84	2·71	2·85	2·52	4·42	5·21	2·66
Magnesia	2·21	3·41	3·23	2·79	2·64	1·72	1·82	1·85
Potash	13·36	14·85	15·13	16·84	10·54	14·25	17·85	16·67
Soda	0·33	0·81	0·48	0·33	0·52	0·72	0·51	0·40
Phosphoric anhydride	4·20	2·98	4·71	5·37	3·56	5·96	3·19	3·16
Sulphuric anhydride	2·05	2·83	3·11	3·63	2·37	3·32	4·76	2·52
Chlorine	1·43	1·86	2·05	2·21	1·08	1·10	2·50	2·80
Silica	72·84	69·82	68·57	65·70	75·98	67·82	64·23	70·09
Total	100·32	100·41	100·46	100·50	100·24	100·25	100·56	100·63
Deduct O = Cl	0·32	0·41	0·46	0·50	0·24	0·25	0·56	0·63
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

Straw, grown at Rothamsted, year after year on the same Land.

Composition of the Ash (excluding Sand and Charcoal), of the Grain, and secutive seasons, 1848–1863.

Plot 3.—Unmanured, every year.

1856	1857	1858	1859	1860	1861	1862	1863	Average.	Harvests.
57·3	78·3	68·3	48·3	50·6	58·7	58·2	70·4	59·5	Grain to 100 straw.
54·3	58·3	60·4	52·5	52·6	57·4	57·8	62·7	57·4	Wt. per bushel of grain, lbs.
Composition of the Grain, per cent.									
82·18	84·91	83·55	82·37	83·10	85·12	82·35	83·97	83·33	Dry matter.
1·91	1·91	1·86	1·96	1·92	2·04	1·76	1·65	1·90	Nitrogen } in dry matter.
2·04	1·92	2·02	2·08	2·16	2·19	2·03	1·95	2·01	Ash (pure) } in dry matter.
Composition of the Grain-Ash, per cent.									
0·87	1·09	1·03	0·96	1·61	1·05	1·32	0·51	1·03	Ferric oxide.
2·55	3·39	2·76	2·75	2·71	2·68	2·54	2·66	2·83	Lime.
10·76	10·81	10·50	10·98	9·14	9·56	10·24	10·91	10·33	Magnesia.
30·55	32·00	32·74	31·94	33·59	34·42	32·33	32·32	32·96	Potash.
0·65	0·42	0·49	0·41	0·74	0·53	1·18	0·76	0·62	Soda.
52·56	50·00	50·85	50·59	47·44	47·47	49·56	51·58	49·71	Phosphoric anhydride.
1·06	1·28	0·66	1·25	2·21	1·66	1·60	0·67	1·31	Sulphuric anhydride.
trace	0·05	none	0·08	0·24	0·15	0·07	none	0·06	Chlorine.
1·00	0·97	0·97	1·06	2·37	2·51	1·18	0·59	1·16	Silica.
100·00	100·01	100·00	100·02	100·05	100·03	100·02	100·00	100·01	Total.
—	0·01	—	0 02	0·05	0·03	0·02	—	0·01	Deduct O = Cl.
100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	Total.
Composition of the Straw, per cent.									
84·17	84·36	85·42	84·52	85·57	85·35	83·58	84·07	83·58	Dry matter.
0·41	0·45	0·45	0·51	0·58	0·63	0·44	0·33	0·50	Nitrogen } in dry matter.
5·87	4·82	5·54	5·33	8·33	6·85	6·89	7·12	6·44	Ash (pure) } in dry matter.
Composition of the Straw-Ash, per cent.									
1·16	1·64	0·67	0·92	1·32	0·32	0·67	0·34	0·84	Ferric oxide.
4·61	2·89	6·10	6·07	4·10	4·28	3·76	4·39	3·89	Lime.
1·70	3·50	2·18	1·59	1·03	1·45	1·30	1·48	2·12	Magnesia.
11·87	15·08	17·29	13·11	11·54	20·68	10·93	13·02	14·56	Potash.
0·59	2·12	0·62	0·64	0·34	0·35	0·35	0·26	0·59	Soda.
4·00	3·51	3·01	3·66	3·48	3·68	3·06	3·16	3·79	Phosphoric anhydride.
3·16	2·73	4·41	3·42	2·39	4·05	2·63	2·87	3·14	Sulphuric anhydride.
1·46	2·16	2·61	1·40	1·14	3·19	1·21	2·04	1·89	Chlorine.
71·78	66·85	63·70	69·50	74·92	62·72	76·37	72·90	69·61	Silica.
100·33	100·48	100·59	100·31	100·26	100·72	100·28	100·46	100·43	Total.
0·33	0·48	0·59	0·31	0·26	0·72	0·28	0·46	0·43	Deduct O = Cl.
100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	Total.

Composition of the Ash of Wheat-Grain, and of Wheat-

Appendix-Table III.—General Characters of the Produce, and *Percentage* of the Straw, in sixteen con-

Plot 10*a*.—*Ammonium-Salts alone, every year.*

Harvests	1848	1849	1850	1851	1852	1853	1854	1855
Grain to 100 straw	56·3	75·1	55·7	64·0	47·3	31·3	61·5	51·2
Weight per bushel of grain, lbs.	58·1	62·3	60·2	61·9	55·9	48·6	60·5	57·1
Composition of the Grain, per cent.								
Dry matter	81·19	82·71	84·33	84·47	83·75	80·45	84·85	84·20
Nitrogen in dry matter	2·42	1·95	2·13	2·15	2·48	2·43	2·30	2·40
Ash (pure) in dry matter	1·95	1·67	1·86	1·81	1·83	1·98	1·72	1·91
Composition of the Grain-Ash, per cent.								
Ferric oxide	1·04	0·79	0·80	0·83	0·64	1·20	0·79	0·75
Lime	3·22	3·46	3·63	3·51	3·51	3·75	3·36	3·57
Magnesia	10·80	10·31	10·70	10·67	12·70	9·34	10·16	10·36
Potash	30·60	35·56	33·19	32·64	28·10	35·88	35·75	34·66
Soda	0·81	0·43	0·28	0·66	0·48	0·78	0·53	0·36
Phosphoric anhydride	51·33	45·87	49·24	49·57	52·92	44·65	46·11	47·53
Sulphuric anhydride	0·78	2·70	1·54	1·46	0·61	2·45	2·23	1·58
Chlorine	trace	0·03	0·03	0·03	trace	0·17	0·45	0·28
Silica	1·42	0·86	0·60	0·64	1·04	1·82	0·72	0·97
Total	100·00	100·01	100·01	100·01	100·00	100·00	100·10	100·06
Deduct O = Cl	—	0·01	0·01	0·01	—	0·04	0·10	0·06
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Composition of the Straw, per cent.								
Dry matter	82·81	83·90	85·66	84·86	83·28	80·94	84·32	83·11
Nitrogen in dry matter	0·82	0·85	0·79	0·74	0·89	1·29	0·56	0·62
Ash (pure) in dry matter	5·43	5·83	5·30	5·42	5·60	5·86	4·54	5·61
Composition of the Straw-Ash, per cent.								
Ferric oxide	0·56	0·78	0·43	0·52	0·75	1·20	0·38	0·29
Lime	5·20	7·00	6·19	5·96	5·60	4·90	5·70	4·66
Magnesia	1·42	2·16	2·18	2·36	1·61	1·32	1·74	1·27
Potash	13·62	14·81	17·43	17·04	10·53	16·89	23·40	22·05
Soda	0·74	1·84	1·73	1·49	1·31	0·87	0·51	0·86
Phosphoric anhydride	3·23	2·71	3·47	3·63	2·50	4·34	2·14	2·10
Sulphuric anhydride	3·08	3·55	4·16	3·27	2·56	3·25	4·77	4·48
Chlorine	1·91	3·30	3·74	4·12	1·54	2·51	5·06	4·52
Silica	70·67	64·59	61·51	62·54	73·96	65·29	57·44	60·79
Total	100·43	100·74	100·84	100·93	100·36	100·57	101·14	101·02
Deduct O = Cl	0·43	0·74	0·84	0·93	0·36	0·57	1·14	1·02
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

Straw, grown at Rothamsted, year after year on the same Land.

Composition of the Ash (excluding Sand and Charcoal), of the Grain, and secutive Seasons, 1848–1863.

Plot 10a.—Ammonium-Salts alone, every year.

1856	1857	1858	1859	1860	1861	1862	1863	Average.	Harvests.
53·4	75·9	67·6	44·2	40·9	44·2	56·2	74·3	57·2	Grain to 100 straw.
55·6	58·0	59·6	51·5	49·5	55·0	56·5	62·6	57·1	Wt. per bushel of grain, lbs.
					Composition of the Grain, per cent.				
83·98	84·93	83·92	82·37	85·03	84·85	83·56	84·80	83·92	Dry matter.
2·23	2·08	2·23	2·30	2·24	2·08	1·89	1·70	2·15	Nitrogen } in dry matter.
1·85	1·63	1·90	1·86	2·12	2·00	1·84	1·56	1·80	Ash (pure) }
					Composition of the Grain-Ash, per cent.				
0·59	1·27	0·63	0·98	1·86	0·69	1·10	0·59	0·91	Ferric oxide.
3·61	4·38	4·05	3·64	3·41	3·47	3·54	3·85	3·62	Lime.
11·41	11·65	10·52	11·23	9·14	9·98	10·73	11·20	10·68	Magnesia.
31·86	31·58	33·52	32·69	34·82	35·54	34·17	34·42	33·43	Potash.
0·37	0·40	0·37	0·73	0·58	0·50	0·92	0·54	0·55	Soda.
50·05	46·99	46·69	47·17	43·35	44·62	44·31	46·02	47·28	Phosphoric anhydride.
1·00	2·12	2·78	2·36	3·57	2·63	2·91	2·37	2·07	Sulphuric anhydride.
none	0·13	0·55	0·04	0·86	1·14	0·67	0·19	0·28	Chlorine.
1·11	1·51	1·01	1·17	2·60	1·68	1·80	0·86	1·24	Silica.
100·00	100·03	100·12	100·01	100·19	100·25	100·15	100·04	100·06	Total.
—	0·03	0·12	0·01	0·19	0·25	0·15	0·04	0·06	Deduct O = Cl.
100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	Total.
					Composition of the Straw, per cent.				
83·34	84·96	85·36	85·24	84·80	84·71	83·37	84·17	84·11	Dry matter.
0·50	0·56	0·63	0·64	0·55	0·71	0·58	0·35	0·67	Nitrogen } in dry matter.
4·58	3·98	4·61	4·29	8·08	5·97	5·45	5·40	5·32	Ash (pure) }
					Composition of the Straw-Ash, per cent.				
0·71	1·05	0·55	0·90	1·09	0·19	0·45	0·22	0·63	Ferric oxide.
5·57	7·79	8·64	8·37	3·32	5·62	5·78	6·92	6·07	Lime.
1·21	1·88	2·44	2·03	1·13	1·91	2·05	1·74	1·78	Magnesia.
13·95	17·50	17·34	13·29	15·37	22·20	13·65	14·25	16·46	Potash.
1·71	0·91	1·16	1·88	0·13	1·81	1·02	0·52	1·15	Soda.
3·33	2·99	3·15	3·54	4·29	2·90	3·35	1·73	3·09	Phosphoric anhydride.
3·98	4·23	7·79	4·55	2·96	4·88	3·44	3·88	4·05	Sulphuric anhydride.
1·59	2·73	2·85	1·78	1·54	3·83	1·68	3·55	2·89	Chlorine.
68·31	61·64	56·73	64·06	70·52	57·52	68·96	67·99	64·53	Silica.
100·36	100·62	100·65	100·40	100·35	100·86	100·38	100·80	100·65	Total.
0·36	0·62	0·65	0·40	0·35	0·86	0·38	0·80	0·65	Deduct O = Cl.
100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	Total.

Composition of the Ash of Wheat-Grain, and of Wheat-

Appendix-Table IV.—General Characters of the Produce, and amounts of 100° C.), of Grain, Straw, and Total Produce, in

Plot 2.—Farmyard Manure, every year.

Harvests		1848	1849	1850	1851	1852	1853	1854	1855
Grain to 100 straw		56·0	68·3	57·3	66·2	49·6	33·2	60·1	58·2
Weight per bushel of grain, lbs.		58·2	63·8	61·9	63·6	58·2	51·1	62·5	62·0
Per 1000 *dry matter of grain.*	Fresh produce	1255	1209	1192	1184	1201	1246	1164	1195
	Nitrogen	18·9	15·8	18·6	15·7	20·2	17·6	17·0	21·9
Ash-constituents, per 1000 *dry matter of grain.*	Ferric oxide	0·25	0·15	0·24	0·17	0·19	0·18	0·12	0·14
	Lime	0·49	0·49	0·57	0·55	0·55	0·57	0·49	0·52
	Magnesia	2·19	2·03	2·27	2·15	2·53	2·23	2·24	2·29
	Potash	6·11	6·37	6·41	6·25	5·38	7·79	6·34	6·43
	Soda	0·11	0·13	0·16	0·10	0·09	0·12	0·10	0·18
	Phosphoric anhydride	10·67	9·70	10·32	9·79	10·83	10·33	10·36	11·08
	Sulphuric anhydride	0·11	0·29	0·29	0·18	0·03	0·52	0·09	0·01
	Chlorine	0·01	0·01	none	trace	trace	0·02	trace	none
	Silica	0·32	0·10	0·19	0·13	0·20	0·20	0·10	0·14
	Total	20·26	19·27	20·45	19·32	19·80	21·96	19·84	20·79
	Deduct O = Cl	—	—	—	—	—	—	—	—
	Total	20·26	19·27	20·45	19·32	19·80	21·96	19·84	20·79
Per 1000 *dry matter of straw.*	Fresh produce	1228	1212	1212	1171	1216	1239	1178	1190
	Nitrogen	4·9	4·5	5·0	4·8	4·6	7·3	3·5	4·3
Ash-constituents, per 1000 *dry matter of straw.*	Ferric oxide	0·38	0·52	0·38	0·30	0·59	0·29	0·16	0·21
	Lime	2·60	3·38	3·27	2·79	2·73	2·14	2·60	2·64
	Magnesia	0·83	1·17	1·34	1·24	1·07	0·91	0·96	0·96
	Potash	10·22	11·41	11·95	11·80	9·06	13·38	9·64	15·54
	Soda	0·18	0·36	0·59	0·36	0·42	0·34	0·23	0·33
	Phosphoric anhydride	2·93	1·98	2·67	3·07	2·27	4·12	1·49	2·88
	Sulphuric anhydride	1·90	2·18	2·27	2·22	1·82	2·36	2·26	1·75
	Chlorine	1·33	1·95	2·39	1·85	1·31	1·77	1·59	3·71
	Silica	44·88	43·92	38·40	43·39	51·47	41·50	30·43	46·78
	Total	65·25	66·87	63·26	67·02	70·74	66·81	49·36	74·80
	Deduct O = Cl	0·30	0·44	0·54	0·42	0·30	0·40	0·36	0·84
	Total	64·95	66·43	62·72	66·60	70·44	66·41	49·00	73·96
Per 1000 *dry matter of total produce (grain and straw).*	Fresh produce	1237	1210	1205	1176	1211	1241	1173	1192
	Nitrogen	9·9	9·1	10·9	9·1	9·8	9·9	8·6	10·8
Ash-constituents, per 1000 *dry matter of total produce (grain and straw.)*	Ferric oxide	0·33	0·37	0·33	0·25	0·46	0·26	0·15	0·18
	Lime	1·85	2·20	2·28	1·91	2·00	1·75	1·80	1·86
	Magnesia	1·31	1·62	1·68	1·60	1·56	1·23	1·44	1·45
	Potash	8·76	9·36	9·91	9·60	7·83	11·99	8·39	12·20
	Soda	0·16	0·27	0·43	0·25	0·31	0·29	0·18	0·27
	Phosphoric anhydride	5·67	5·12	5·49	5·73	5·13	5·67	4·84	5·89
	Sulphuric anhydride	1·27	1·41	1·54	1·41	1·22	1·90	1·44	1·11
	Chlorine	0·87	1·16	1·51	1·12	0·87	1·34	0·99	2·35
	Silica	29·09	26·11	24·32	26·26	34·31	31·24	18·96	29·67
	Total	49·31	47·52	47·49	48·13	53·69	55·67	38·19	54·98
	Deduct O = Cl	0·20	0·26	0·34	0·25	0·20	0·30	0·22	0·53
	Total	49·11	47·26	47·15	47·88	53·49	55·37	37·97	54·45

Straw, grown at Rothamsted, year after year on the same Land.

Nitrogen, Ash-Constituents, and Total Ash (pure), *per* 1000 *Dry Matter* (at sixteen consecutive Seasons, 1848–1863.

Plot 2.—*Farmyard Manure, every year.*

1856	1857	1858	1859	1860	1861	1862	1863	Average.	Harvests.
52·8	77·9	65·5	47·1	54·2	71·0	58·3	67·5	58·6	Grain to 100 straw.
58·6	60·4	62·6	56·5	55·5	60·5	61·0	63·1	60·0	Wt. per bushel of grain, lbs.
1211	1124	1197	1209	1169	1181	1201	1182	1194	Fresh produce.
18·9	19·7	19·1	20·9	20·0	19·5	15·7	15·2	18·3	Nitrogen.
0·17	0·20	0·19	0·16	0·22	0·11	0·15	0·08	0·16	Ferric oxide.
0·50	0·56	0·53	0·50	0·60	0·54	0·50	0·43	0·52	Lime.
2·32	2·32	2·28	2·36	2·18	2·21	2·22	2·12	2·24	Magnesia.
5·80	5·79	6·52	6·58	7·27	7·12	6·37	5·85	6·35	Potash.
0·08	0·15	0·06	0·11	0·14	0·14	0·13	0·12	0·12	Soda.
10·73	10·18	10·61	11·10	10·65	11·05	10·28	9·65	10·44	Phosphoric anhydride.
0·05	0·09	0·15	0·11	0·19	0·22	0·10	0·17	0·15	Sulphuric anhydride.
0·01	trace	0·01	trace	0·02	none	none	trace	0·01	Chlorine.
0·15	0·10	0·10	0·17	0·27	0·11	0·16	0·12	0·15	Silica.
19·81	19·39	20·45	21·09	21·54	21·50	19·91	18·54	20·14	Total.
—	—	—	—	—	—	—	—	—	Deduct O = Cl.
19·81	19·39	20·45	21·09	21·54	21·50	19·91	18·54	20·14	Total.
1204	1185	1174	1181	1176	1165	1192	1184	1193	Fresh produce.
3·8	3·9	4·7	4·0	5·6	4·3	3·7	2·5	4·4	Nitrogen.
0·32	0·44	0·28	0·38	0·66	0·16	0·26	0·12	0·33	Ferric oxide.
2·61	2·98	2·59	2·85	2·53	2·44	2·16	2·43	2·66	Lime.
1·03	0·88	1·09	0·83	0·84	0·86	0·90	0·91	0·98	Magnesia.
9·60	10·96	13·92	11·63	13·21	18·37	9·73	11·53	11·91	Potash.
0·35	0·24	0·31	0·34	0·40	0·51	0·36	none	0·32	Soda.
2·25	1·89	2·19	2·19	3·20	2·59	2·20	2·02	2·45	Phosphoric anhydride.
1·72	1·46	2·28	1·27	2·01	2·51	1·53	1·63	1·92	Sulphuric anhydride.
1·50	2·19	3·09	1·74	1·54	3·57	1·24	2·32	2·06	Chlorine.
46·64	33·98	39·10	41·57	55·05	41·48	48·84	43·74	43·08	Silica.
66·02	55·02	64·85	62·80	79·44	72·49	67·22	64·70	65·71	Total.
0·34	0·49	0·69	0·39	0·35	0·81	0·28	0·52	0·46	Deduct O = Cl.
65·68	54·53	64·16	62·41	79·09	71·68	66·94	64·18	65·25	Total.
1206	1178	1183	1190	1174	1172	1195	1183	1193	Fresh produce.
9·0	10·9	10·3	9·3	10·7	10·5	8·1	7·6	9·5	Nitrogen.
0·27	0·34	0·24	0·31	0·50	0·14	0·22	0·10	0·27	Ferric oxide.
1·89	1·91	1·78	2·11	1·85	1·66	1·55	1·63	1·87	Lime.
1·48	1·51	1·56	1·31	1·31	1·42	1·38	1·39	1·45	Magnesia.
8·29	8·68	11·03	10·04	11·12	13·73	8·50	9·24	9·85	Potash.
0·28	0·20	0·21	0·26	0·31	0·36	0·28	0·05	0·25	Soda.
5·17	5·55	5·48	5·00	5·83	6·07	5·16	5·10	5·40	Phosphoric anhydride.
1·14	0·85	1·45	0·91	1·37	1·56	1·01	1·04	1·27	Sulphuric anhydride.
0·99	1·22	1·88	1·19	1·01	2·10	0·78	1·38	1·30	Chlorine.
30·64	19·04	23·86	28·54	35·72	24·44	30·99	26·15	27·23	Silica.
50·13	39·30	47·49	49·67	59·02	51·48	49·87	46·08	48·89	Total.
0·23	0·27	0·42	0·27	0·23	0·47	0·18	0·31	0·29	Deduct O = Cl.
49·90	39·03	47·07	49·40	58·79	51·01	49·69	45·77	48·60	Total.

Composition of the Ash of Wheat-Grain, and of Wheat-

Appendix-Table V.—General Characters of the Produce, and amounts of 100° C.), of Grain, Straw, and Total Produce, in

Plot 3.—Unmanured, every year.

Harvests...	1848	1849	1850	1851	1852	1853	1854	1855
Grain to 100 straw	55·6	76·1	58·2	66·6	53·9	25·4	63·6	60·0
Weight per bushel of grain, lbs.	57·3	61·4	60·6	61·1	56·6	45·9	60·6	59·2
Per 1000 dry matter of grain. Fresh produce	1244	1216	1193	1186	1211	1247	1181	1179
Per 1000 dry matter of grain. Nitrogen	21·7	17·3	18·3	16·7	20·8	20·9	19·2	21·4
Ash-constituents, per 1000 dry matter of grain. Ferric oxide	0·28	0·20	0·26	0·14	0·22	0·30	0·12	0·12
Lime	0·57	0·59	0·60	0·58	0·58	0·73	0·52	0·53
Magnesia	2·07	1·83	1·99	1·97	2·36	2·43	2·04	2·01
Potash	6·25	6·65	6·65	6·75	6·01	8·38	6·67	6·86
Soda	0·13	0·08	0·18	0·09	0·13	0·13	0·14	0·10
Phosphoric anhydride	10·29	8·98	10·02	9·53	10·50	10·75	9·64	10·27
Sulphuric anhydride	0·16	0·34	0·23	0·22	0·20	0·57	0·31	0·13
Chlorine	trace	trace	0·01	0·01	0·01	0·04	trace	0·01
Silica	0·27	0·14	0·23	0·14	0·27	0·30	0·09	0·19
Total	20·02	18·81	20·17	19·43	20·28	23·63	19·53	20·22
Deduct O = Cl	—	—	—	—	—	0·01	—	—
Total	20·02	18·81	20·17	19·43	20·28	23·62	19·53	20·22
Per 1000 dry matter of straw. Fresh produce	1234	1218	1211	1186	1194	1226	1201	1207
Per 1000 dry matter of straw. Nitrogen	5·3	4·9	5·3	5·7	5·7	8·5	3·9	4·8
Ash-constituents, per 1000 dry matter of straw. Ferric oxide	0·76	0·70	0·33	0·52	0·73	0·59	0·25	0·35
Lime	1·88	2·00	1·91	1·86	1·77	2·77	2·69	1·94
Magnesia	1·50	2·40	2·27	1·83	1·85	1·08	0·94	1·35
Potash	9·04	10·43	10·64	11·02	7·43	8·94	9·22	12·17
Soda	0·23	0·57	0·34	0·22	0·36	0·45	0·26	0·29
Phosphoric anhydride	2·83	2·09	3·31	3·51	2·52	3·74	1·65	2·30
Sulphuric anhydride	1·39	1·99	2·19	2·37	1·67	2·09	2·46	1·84
Chlorine	0·97	1·31	1·44	1·45	0·76	0·70	1·30	2·04
Silica	49·28	49·05	48·22	43·00	53·51	42·54	33·17	51·14
Total	67·88	70·54	70·65	65·78	70·60	62·90	51·94	73·42
Deduct O = Cl	0·22	0·29	0·32	0·33	0·17	0·16	0·29	0·46
Total	67·66	70·25	70·33	65·45	70·43	62·74	51·65	72·96
Per 1000 dry matter of total produce (grain and straw). Fresh produce	1238	1217	1204	1186	1209	1230	1193	1197
Per 1000 dry matter of total produce (grain and straw). Nitrogen	11·2	10·3	10·1	10·1	11·0	11·0	9·9	11·1
Ash-constituents, per 1000 dry matter of total produce (grain and straw). Ferric oxide	0·58	0·49	0·31	0·37	0·55	0·53	0·20	0·26
Lime	1·42	1·39	1·42	1·35	1·36	2·37	1·84	1·40
Magnesia	1·70	2·15	2·17	1·89	2·03	1·35	1·37	1·60
Potash	8·05	8·79	9·16	9·31	6·93	8·83	8·22	10·15
Soda	0·19	0·36	0·28	0·17	0·28	0·38	0·22	0·22
Phosphoric anhydride	5·49	5·07	5·80	5·92	5·31	5·14	4·78	5·34
Sulphuric anhydride	0·95	1·28	1·46	1·51	1·16	1·78	1·61	1·19
Chlorine	0·63	0·74	0·91	0·87	0·50	0·57	0·79	1·27
Silica	31·86	27·88	30·38	25·87	34·90	34·10	20·18	31·75
Total	50·87	48·15	51·89	47·26	53·02	55·05	39·21	53·18
Deduct O = Cl	0·14	0·16	0·21	0·20	0·11	0·13	0·18	0·29
Total	50·73	47·99	51·68	47·06	52·91	54·92	39·03	52·89

Straw, grown at Rothamsted, year after year on the same Land.

Nitrogen, Ash-Constituents, and Total Ash (pure), *per* 1000 *Dry Matter* (at sixteen consecutive Seasons, 1848–1863.

Plot 3.—*Unmanured, every year.*

1856	1857	1858	1859	1860	1861	1862	1863	Average.	Harvests.
57·3	78·3	68·3	48·3	50·6	58·7	58·2	70·4	59·5	Grain to 100 straw.
54·3	58·3	60·4	52·5	52·6	57·4	57·8	62·7	57·4	Wt. per bushel of grain, lbs.
1217	1178	1197	1214	1204	1176	1215	1191	1200	Fresh produce.
19·1	19·1	18·6	19·6	19·2	20·4	17·6	16·5	19·0	Nitrogen.
0·18	0·21	0·21	0·20	0·35	0·23	0·27	0·10	0·20	Ferric oxide.
0·52	0·65	0·56	0·57	0·59	0·59	0·51	0·52	0·57	Lime.
2·19	2·08	2·12	2·28	1·98	2·09	2·08	2·12	2·08	Magnesia.
6·23	6·16	6·61	6·64	7·26	7·54	6·56	6·28	6·62	Potash.
0·13	0·08	0·10	0·09	0·16	0·12	0·24	0·15	0·13	Soda.
10·72	9·62	10·27	10·52	10·25	10·39	10·05	10·03	10·03	Phosphoric anhydride.
0·22	0·25	0·13	0·26	0·48	0·36	0·33	0·13	0·25	Sulphuric anhydride.
trace	0·01	none	0·02	0·05	0·03	0·02	none	0·01	Chlorine.
0·20	0·19	0·20	0·22	0·51	0·55	0·24	0·12	0·22	Silica.
20·39	19·25	20·20	20·80	21·63	21·90	20·30	19·45	20·11	Total.
—	—	—	—	0·01	0·01	—	—	—	Deduct O = Cl.
20·39	19·25	20·20	20·80	21·62	21·89	20·30	19·45	20·11	Total.
1188	1185	1171	1183	1169	1172	1196	1190	1196	Fresh produce.
4·1	4·5	4·5	5·1	5·8	6·3	4·4	3·3	5·0	Nitrogen.
0·69	0·79	0·37	0·49	1·10	0·22	0·47	0·24	0·53	Ferric oxide.
2·70	1·39	3·38	3·23	3·42	2·93	2·58	3·13	2·48	Lime.
0·99	1·69	1·21	0·85	0·86	0·99	0·89	1·06	1·35	Magnesia.
6·96	7·26	9·59	6·98	9·61	14·16	7·53	9·27	9·30	Potash.
0·35	1·02	0·34	0·34	0·28	0·24	0·24	0·18	0·35	Soda.
2·35	1·69	1·67	1·95	2·90	2·52	2·11	2·25	2·42	Phosphoric anhydride.
1·86	1·32	2·45	1·62	1·99	2·77	1·81	2·03	2·00	Sulphuric anhydride.
0·86	1·04	1·44	0·75	0·95	2·19	0·83	1·45	1·21	Chlorine.
42·11	32·19	35·31	37·02	62·40	42·94	52·59	51·92	45·00	Silica.
58·87	48·39	55·76	53·43	83·51	68·96	69·05	71·53	64·64	Total.
0·20	0·23	0·33	0·17	0·21	0·49	0·19	0·33	0·27	Deduct O = Cl.
58·67	48·16	55·43	53·26	83·30	68·47	68·86	71·20	64·37	Total.
1198	1182	1182	1193	1181	1173	1203	1190	1198	Fresh produce.
9·5	10·9	10·1	9·8	10·2	11·5	9·2	8·7	10·3	Nitrogen.
0·51	0·54	0·31	0·39	0·85	0·22	0·39	0·18	0·41	Ferric oxide.
1·92	1·07	2·25	2·38	2·49	2·07	1·83	2·05	1·77	Lime.
1·42	1·86	1·57	1·31	1·23	1·40	1·33	1·50	1·62	Magnesia.
6·70	6·77	8·40	6·87	8·83	11·72	7·18	8·04	8·30	Potash.
0·27	0·60	0·24	0·26	0·24	0·19	0·24	0·17	0·27	Soda.
5·35	5·19	5·12	4·70	5·32	5·42	5·00	5·46	5·26	Phosphoric anhydride.
1·27	0·84	1·52	1·32	1·49	1·89	1·27	1·25	1·35	Sulphuric anhydride.
0·55	0·59	0·87	0·51	0·66	1·39	0·53	0·85	0·76	Chlorine.
27·09	18·09	21·24	25·24	42·02	27·29	33·53	30·53	28·32	Silica.
45·08	35·55	41·52	42·98	63·13	51·59	51·30	50·03	48·06	Total.
0·13	0·13	0·20	0·11	0·15	0·31	0·13	0·19	0·17	Deduct O = Cl.
44·95	35·42	41·32	42·87	62·98	51·28	51·17	49·84	47·89	Total.

Composition of the Ash of Wheat-Grain, and of Wheat-

Appendix-Table VI.—General Characters of the Produce, Amounts of Nitrogen, Grain, Straw, and Total Produce, in sixteen

Plot 10a.—Ammonium-Salts alone, every year.

Harvests		1848	1849	1850	1851	1852	1853	1854	1855
Grain to 100 straw		56·3	75·1	55·7	64·0	47·3	31·3	61·5	51·2
Weight per bushel of grain, lbs.		58·1	62·3	60·2	61·9	55·9	48·6	60·5	57·1
Per 1000 dry matter of grain.	Fresh produce	1232	1209	1186	1184	1193	1242	1178	1188
	Nitrogen	24·2	19·5	21·3	21·5	24·8	24·3	23·0	24·0
Ash-constituents, per 1000 dry matter of grain.	Ferric oxide	0·20	0·13	0·15	0·15	0·12	0·24	0·14	0·14
	Lime	0·63	0·58	0·68	0·64	0·64	0·74	0·58	0·68
	Magnesia	2·11	1·72	1·99	1·93	2·33	1·85	1·74	1·97
	Potash	5·98	5·93	6·18	5·89	5·15	7·09	6·15	6·61
	Soda	0·16	0·07	0·05	0·12	0·09	0·15	0·09	0·07
	Phosphoric anhydride	10·03	7·66	9·16	8·96	9·69	8·82	7·93	9·06
	Sulphuric anhydride	0·15	0·45	0·29	0·26	0·11	0·49	0·38	0·30
	Chlorine	trace	0·01	0·01	0·01	trace	0·03	0·08	0·05
	Silica	0·28	0·14	0·11	0·11	0·19	0·36	0·12	0·18
	Total	19·54	16·69	18·62	18·07	18·32	19·77	17·21	19·06
	Deduct O = Cl	—	—	—	—	—	0·01	0·02	0·01
	Total	19·54	16·69	18·62	18·07	18·32	19·76	17·19	19·05
Per 1000 dry matter of straw.	Fresh produce	1208	1192	1167	1178	1200	1236	1186	1204
	Nitrogen	8·2	8·5	7·8	7·4	8·9	12·9	5·6	6·2
Ash-constituents, per 1000 dry matter of straw.	Ferric oxide	0·30	0·45	0·23	0·29	0·42	0·70	0·17	0·17
	Lime	2·83	4·08	3·28	3·23	3·13	2·87	2·59	2·62
	Magnesia	0·77	1·26	1·16	1·28	0·90	0·78	0·79	0·71
	Potash	7·40	8·62	9·23	9·23	5·89	9·89	10·63	12·36
	Soda	0·40	1·07	0·91	0·80	0·74	0·51	0·23	0·48
	Phosphoric anhydride	1·76	1·58	1·84	1·97	1·40	2·54	0·97	1·17
	Sulphuric anhydride	1·67	2·07	2·20	1·78	1·43	1·90	2·16	2·52
	Chlorine	1·04	1·92	1·98	2·23	0·87	1·47	2·30	2·54
	Silica	38·41	37·63	32·58	33·88	41·39	38·24	26·09	34·09
	Total	54·58	58·68	53·41	54·69	56·17	58·90	45·93	56·66
	Deduct O = Cl	0·23	0·43	0·44	0·51	0·20	0·33	0·52	0·57
	Total	54·35	58·25	52·97	54·18	55·97	58·57	45·41	56·09
Per 1000 dry matter of total produce (grain and straw).	Fresh produce	1216	1199	1174	1180	1196	1237	1183	1198
	Nitrogen	13·9	13·2	12·6	12·9	14·0	15·6	12·3	12·3
Ash-constituents, per 1000 dry matter of total produce (grain and straw.)	Ferric oxide	0·27	0·32	0·20	0·23	0·32	0·59	0·16	0·16
	Lime	2·04	2·59	2·36	2·22	2·33	2·37	1·82	1·95
	Magnesia	1·25	1·46	1·45	1·53	1·36	1·03	1·15	1·14
	Potash	6·89	7·48	8·15	7·93	5·65	9·23	8·91	10·40
	Soda	0·32	0·65	0·61	0·54	0·53	0·43	0·18	0·34
	Phosphoric anhydride	4·70	4·16	4·44	4·69	4·08	4·03	3·63	3·86
	Sulphuric anhydride	1·13	1·38	1·52	1·19	1·00	1·56	1·48	1·76
	Chlorine	0·67	1·11	1·28	1·37	0·59	1·13	1·45	1·69
	Silica	24·84	21·67	21·08	20·74	28·10	29·23	16·16	22·52
	Total	42·11	40·82	41·09	40·44	43·96	49·60	34·94	43·82
	Deduct O = Cl	0·15	0·25	0·29	0·31	0·14	0·26	0·32	0·38
	Total	41·96	40·57	40·80	40·13	43·82	49·34	34·62	43·44

Straw, grown at Rothamsted, year after year on the same Land.

Ash-Constituents, and Total Ash (pure), *per* 1000 *Dry Matter* (at 100° C.), of consecutive Seasons, 1848–1863.

Plot 10*a*.—*Ammonium-Salts alone, every year.*

1856	1857	1858	1859	1860	1861	1862	1863	Average.	Harvests.
53·4	75·9	67·6	44·2	40·9	44·2	56·2	74·3	57·2	Grain to 100 straw.
55·6	58·0	59·6	51·5	49·5	55·0	56·5	62·6	57·1	Wt. per bushel of grain, lbs.
1191	1178	1191	1214	1175	1178	1197	1179	1191	Fresh produce.
22·3	20·8	22·3	23·0	22·4	20·8	18·9	17·0	21·5	Nitrogen.
0·11	0·21	0·12	0·18	0·39	0·14	0·20	0·09	0·16	Ferric oxide.
0·67	0·72	0·77	0·68	0·72	0·69	0·65	0·60	0·65	Lime.
2·11	1·90	1·99	2·09	1·94	2·00	1·98	1·75	1·93	Magnesia.
5·88	5·16	6·35	6·09	7·38	7·12	6·30	5·37	6·02	Potash.
0·07	0·07	0·07	0·14	0·12	0·10	0·17	0·09	0·10	Soda.
9·25	7·67	8·85	8·78	9·18	8·94	8·17	7·18	8·54	Phosphoric anhydride.
0·19	0·34	0·53	0·44	0·76	0·53	0·54	0·37	0·37	Sulphuric anhydride.
none	0·02	0·11	0·01	0·18	0·23	0·12	0·03	0·04	Chlorine.
0·20	0·25	0·19	0·22	0·55	0·34	0·33	0·13	0·21	Silica.
18·48	16·34	18·98	18·63	21·22	20·09	18·46	15·61	18·02	Total.
—	—	0·02	—	0·04	0·05	0·03	0·01	0·01	Deduct O = Cl.
18·48	16·34	18·96	18·63	21·18	20·04	18·43	15·60	18·01	Total.
1201	1177	1171	1173	1180	1180	1199	1188	1189	Fresh produce.
5·0	5·6	6·3	6·4	5·5	7·1	5·8	3·5	6·7	Nitrogen.
0·32	0·42	0·26	0·39	0·88	0·12	0·24	0·12	0·33	Ferric oxide.
2·55	3·10	3·98	3·59	2·68	3·36	3·15	3·74	3·18	Lime.
0·55	0·75	1·13	0·87	0·91	1·14	1·12	0·94	0·94	Magnesia.
6·39	6·97	8·00	5·69	12·42	13·24	7·44	7·70	8·71	Potash.
0·79	0·32	0·54	0·81	0·10	1·08	0·55	0·29	0·60	Soda.
1·53	1·19	1·45	1·52	3·47	1·73	1·83	0·93	1·63	Phosphoric anhydride.
1·82	1·69	3·60	1·95	2·39	2·91	1·88	2·09	2·10	Sulphuric anhydride.
0·73	1·09	1·31	0·76	1·25	2·29	0·92	1·92	1·57	Chlorine.
31·27	24·53	26·16	27·45	57·01	34·32	37·59	36·74	34·49	Silica.
45·95	40·06	46·43	43·03	81·11	60·19	54·72	54·47	53·55	Total.
0·16	0·25	0·30	0·17	0·28	0·51	0·20	0·43	0·35	Deduct O = Cl.
45·79	39·81	46·13	42·86	80·83	59·68	54·52	54·04	53·20	Total.
1197	1177	1179	1185	1178	1180	1199	1184	1190	Fresh produce.
11·0	12·2	12·7	11·4	10·4	11·3	10·5	9·3	12·1	Nitrogen.
0·25	0·33	0·20	0·32	0·74	0·12	0·23	0·11	0·27	Ferric oxide.
1·89	2·07	2·70	2·71	2·11	2·54	2·25	2·40	2·26	Lime.
1·10	1·24	1·47	1·24	1·21	1·40	1·43	1·28	1·30	Magnesia.
6·21	6·19	7·35	5·81	10·95	11·36	7·03	6·70	7·74	Potash.
0·53	0·21	0·35	0·61	0·11	0·78	0·42	0·20	0·42	Soda.
4·23	3·99	4·41	3·70	5·13	3·95	4·11	3·61	4·14	Phosphoric anhydride.
1·25	1·11	2·37	1·50	1·92	2·18	1·39	1·35	1·47	Sulphuric anhydride.
0·47	0·63	0·83	0·54	0·94	1·66	0·63	1·11	1·01	Chlorine.
20·40	14·06	15·80	19·30	40·58	23·88	24·17	21·07	22·03	Silica.
36·33	29·83	35·48	35·73	63·69	47·87	41·66	37·83	40·64	Total.
0·11	0·14	0·19	0·12	0·21	0·37	0·14	0·25	0·23	Deduct O = Cl.
36·22	29·69	35·29	35·61	63·48	47·50	41·52	37·58	40·41	Total.

Composition of the Ash of Wheat-Grain, and of Wheat-

Appendix-Table VII.—General Characters of the Produce, and Quantities of (pure), *per Acre*, in Grain, Straw, and Total

Plot 2.—Farmyard Manure, every year.

		1848	1849	1850	1851	1852	1853	1854	1855
Harvests									
Grain to 100 straw		56·0	68·3	57·3	66·2	49·6	33·2	60·1	58·2
Weight per bushel of grain, lbs.		58·2	63·8	61·9	63·6	58·2	51·1	62·5	62·0
Produce of grain, per acre, lbs.	Fresh produce	1705	2068	1861	2049	1716	1120	2675	2237
	Dry matter	1359	1712	1561	1731	1429	899	2298	1872
	Nitrogen	25·7	27·0	29·0	27·2	28·9	15·8	39·1	41·0
Ash-constituents of grain, per acre, lbs.	Ferric oxide	0·34	0·25	0·37	0·29	0·27	0·16	0·28	0·27
	Lime	0·66	0·83	0·90	0·96	0·79	0·51	1·12	0·97
	Magnesia	2·97	3·48	3·53	3·72	3·61	2·00	5·14	4·29
	Potash	8·30	10·91	10·01	10·82	7·70	7·00	14·58	12·03
	Soda	0·16	0·22	0·26	0·17	0·13	0·11	0·22	0·33
	Phosphoric anhydride	14·49	16·60	16·11	16·95	15·47	9·29	23·80	20·74
	Sulphuric anhydride	0·15	0·50	0·45	0·31	0·04	0·47	0·21	0·01
	Chlorine	0·02	0·01	none	trace	trace	0·02	0·01	none
	Silica	0·43	0·18	0·29	0·22	0·28	0·18	0·23	0·27
	Total	27·52	32·98	31·92	33·44	28·29	19·74	45·59	38·91
	Deduct O = Cl	—	—	—	—	—	—	—	—
	Total	27·52	32·98	31·92	33·44	28·29	19·74	45·59	38·91
Produce of straw, per acre, lbs.	Fresh produce	3041	3029	3245	3094	3457	3372	4450	3845
	Dry matter	2477	2499	2677	2642	2842	2721	3778	3230
	Nitrogen	12·1	11·2	13·4	12·7	13·1	19·9	13·2	13·9
Ash-constituents of straw, per acre, lbs.	Ferric oxide	0·94	1·30	1·02	0·79	1·69	0·78	0·62	0·68
	Lime	6·45	8·43	8·76	7·38	7·76	5·83	9·83	8·53
	Magnesia	2·05	2·93	3·59	3·29	3·04	2·47	3·63	3·11
	Potash	25·31	28·52	31·98	31·16	25·76	36·39	36·41	50·20
	Soda	0·45	0·91	1·57	0·95	1·19	0·93	0·86	1·07
	Phosphoric anhydride	7·26	4·94	7·16	8·10	6·44	11·22	5·62	9·31
	Sulphuric anhydride	4·70	5·44	6·07	5·87	5·16	6·42	8·54	5·64
	Chlorine	3·30	4·88	6·41	4·88	3·72	4·83	6·00	11·98
	Silica	111·16	109·76	102·78	114·63	146·27	112·92	114·96	151·10
	Total	161·62	167·11	169·34	177·05	201·03	181·79	186·47	241·62
	Deduct O = Cl	0·74	1·09	1·45	1·11	0·84	1·08	1·36	2·70
	Total	160·88	166·02	167·89	175·94	200·19	180·71	185·11	238·92
Total produce (grain and straw), per acre, lbs.	Fresh produce	4746	5097	5106	5143	5173	4492	7125	6082
	Dry matter	3836	4211	4238	4373	4271	3620	6076	5102
	Nitrogen	37·8	38·2	42·4	39·9	42·0	35·7	52·3	54·9
Ash-constituents of total produce (grain and straw), per acre, lbs.	Ferric oxide	1·28	1·55	1·39	1·08	1·96	0·94	0·90	0·95
	Lime	7·11	9·26	9·66	8·34	8·55	6·34	10·95	9·50
	Magnesia	5·02	6·41	7·12	7·01	6·65	4·47	8·77	7·40
	Potash	33·61	39·43	41·99	41·98	33·46	43·39	50·99	62·23
	Soda	0·61	1·13	1·83	1·12	1·32	1·04	1·08	1·40
	Phosphoric anhydride	21·75	21·54	23·27	25·05	21·91	20·51	29·42	30·05
	Sulphuric anhydride	4·85	5·94	6·52	6·18	5·20	6·89	8·75	5·65
	Chlorine	3·32	4·89	6·41	4·88	3·72	4·85	6·01	11·98
	Silica	111·59	109·94	103·07	114·85	146·55	113·10	115·19	151·37
	Total	189·14	200·09	201·26	210·49	229·32	201·53	232·06	280·53
	Deduct O = Cl	0·74	1·09	1·45	1·11	0·84	1·08	1·36	2·70
	Total	188·40	199·00	199·81	209·38	228·48	200·45	230·70	277·83

Straw, grown at Rothamsted, year after year on the same Land.

Fresh Produce, Dry Matter, Nitrogen, Ash-Constituents, and Total Ash Produce, in sixteen consecutive Seasons, 1848–1863.

Plot 2.—Farmyard Manure, every year.

1856	1857	1858	1859	1860	1861	1862	1863	Average.	Harvests.
52·8	77·9	65·5	47·1	54·2	71·0	58·3	67·5	58·6	Grain to 100 straw.
58·6	60·4	62·6	56·5	55·5	60·5	61·0	63·1	60·0	Wt. per bushel of grain, lbs.
2277	2587	2512	2263	1864	2202	2447	2886	2154	Fresh produce.
1881	2212	2099	1872	1594	1864	2038	2442	1804	Dry matter.
35·6	43·6	40·1	39·1	31·9	36·3	32·0	37·1	33·1	Nitrogen.
0·32	0·45	0·39	0·31	0·35	0·19	0·31	0·20	0·30	Ferric oxide.
0·94	1·24	1·12	0·94	0·95	1·01	1·02	1·06	0·94	Lime.
4·36	5·13	4·79	4·42	3·48	4·13	4·52	5·17	4·04	Magnesia.
10·91	12·80	13·68	12·31	11·60	13·27	12·98	14·28	11·45	Potash.
0·16	0·33	0·12	0·21	0·23	0·26	0·27	0·30	0·22	Soda.
20·19	22·52	22·27	20·79	16·96	20·60	20·94	23·55	18·83	Phosphoric anhydride.
0·09	0·20	0·32	0·20	0·30	0·41	0·21	0·42	0·27	Sulphuric anhydride.
0·03	trace	0·03	trace	0·02	none	none	trace	0·01	Chlorine.
0·28	0·21	0·21	0·31	0·44	0·20	0·33	0·29	0·27	Silica.
37·28	42·88	42·93	39·49	34·33	40·07	40·58	45·27	36·33	Total.
0·01	—	0·01	—	—	—	—	—	—	Deduct O = Cl.
37·27	42·88	42·92	39·49	34·33	40·07	40·58	45·27	36·33	Total.
4317	3323	3837	4810	3440	3101	4195	4279	3677	Fresh produce.
3587	2805	3269	4073	2924	2662	3519	3613	3082	Dry matter.
13·6	10·9	15·4	16·3	16·4	11·4	13·0	9·0	13·5	Nitrogen.
1·15	1·23	0·92	1·55	1·93	0·44	0·91	0·42	1·02	Ferric oxide.
9·38	8·35	8·46	11·59	7·40	6·48	7·61	8·77	8·19	Lime.
3·71	2·47	3·55	3·38	2·45	2·29	3·16	3·27	3·03	Magnesia.
34·44	30·75	45·50	47·35	38·63	48·89	34·23	41·68	36·70	Potash.
1·25	0·68	1·03	1·36	1·17	1·37	1·27	none	1·00	Soda.
8·06	5·30	7·15	8·94	9·35	6·89	7·73	7·32	7·55	Phosphoric anhydride.
6·16	4·08	7·47	5·19	5·88	6·68	5·39	5·88	5·91	Sulphuric anhydride.
5·38	6·14	10·08	7·08	4·52	9·50	4·36	8·37	6·34	Chlorine.
167·29	95·32	127·84	169·33	160·96	110·42	171·89	158·03	132·79	Silica.
236·82	154·32	212·00	255·77	232·29	192·96	236·55	233·74	202·53	Total.
1·23	1·37	2·27	1·60	1·02	2·16	0·98	1·88	1·43	Deduct O = Cl.
235·59	152·95	209·73	254·17	231·27	190·80	235·57	231·86	201·10	Total.
6594	5910	6349	7073	5304	5303	6642	7165	5831	Fresh produce.
5468	5017	5368	5945	4518	4526	5557	6055	4886	Dry matter.
49·2	54·5	55·5	55·4	48·3	47·7	45·0	46·1	46·6	Nitrogen.
1·47	1·68	1·31	1·86	2·28	0·63	1·22	0·62	1·32	Ferric oxide.
10·32	9·59	9·58	12·53	8·35	7·49	8·63	9·83	9·13	Lime.
8·07	7·60	8·34	7·80	5·93	6·42	7·68	8·44	7·07	Magnesia.
45·35	43·55	59·18	59·66	50·23	62·16	47·21	55·96	48·15	Potash.
1·41	1·01	1·15	1·57	1·40	1·63	1·54	0·30	1·22	Soda.
28·25	27·82	29·42	29·73	26·31	27·49	28·67	30·87	26·38	Phosphoric anhydride.
6·25	4·28	7·79	5·39	6·18	7·09	5·60	6·30	6·18	Sulphuric anhydride.
5·41	6·14	10·11	7·08	4·54	9·50	4·36	8·37	6·35	Chlorine.
167·57	95·53	128·05	169·64	161·40	110·62	172·22	158·32	133·06	Silica.
274·11	197·20	254·93	295·26	266·62	233·03	277·13	279·01	238·86	Total.
1·24	1·37	2·28	1·60	1·02	2·16	0·98	1·88	1·43	Deduct O = Cl.
272·86	195·83	252·65	293·66	265·60	230·87	276·15	277·13	237·43	Total.

Composition of the Ash of Wheat-Grain, and of Wheat-

Appendix-Table VIII.—General Characters of the Produce, and Quantities of (pure), *per Acre*, in Grain, Straw, and Total Pro-

Plot 3.—Unmanured, every year.

Harvests		1848	1849	1850	1851	1852	1853	1854	1855
Grain to 100 straw		55·6	76·1	58·2	66·6	53·9	25·4	63·6	60·0
Weight per bushel of grain, lbs.		57·3	61·4	60·6	61·1	56·6	45·9	60·6	59·2
Produce of grain, per acre, lbs.	Fresh produce	952	1229	1002	1083	860	359	1359	1072
	Dry matter	765	1011	840	913	710	288	1151	909
	Nitrogen	16·6	17·5	15·4	15·2	14·8	6·0	22·1	19·5
Ash-constituents of grain, per acre, lbs.	Ferric oxide	0·21	0·20	0·22	0·13	0·16	0·09	0·14	0·11
	Lime	0·44	0·60	0·50	0·53	0·41	0·21	0·60	0·49
	Magnesia	1·59	1·85	1·67	1·80	1·68	0·70	2·35	1·83
	Potash	4·78	6·72	5·58	6·16	4·27	2·41	7·68	6·23
	Soda	0·10	0·08	0·16	0·08	0·09	0·04	0·16	0·09
	Phosphoric anhydride	7·87	9·08	8·42	8·70	7·45	3·10	11·09	9·33
	Sulphuric anhydride	0·12	0·35	0·19	0·20	0·14	0·16	0·35	0·12
	Chlorine	trace	trace	0·01	0·01	0·01	0·01	0·01	0·01
	Silica	0·21	0·14	0·19	0·13	0·19	0·08	0·10	0·17
	Total	15·32	19·02	16·94	17·74	14·40	6·80	22·48	18·38
	Deduct O = Cl	—	—	—	—	—	—	—	—
	Total	15·32	19·02	16·94	17·74	14·40	6·80	22·48	18·38
Produce of straw, per acre, lbs.	Fresh produce	1712	1614	1719	1627	1597	1413	2137	1787
	Dry matter	1387	1325	1420	1372	1322	1153	1780	1480
	Nitrogen	7·4	6·5	7·5	7·8	7·5	9·8	6·9	7·1
Ash-constituents of straw, per acre, lbs.	Ferric oxide	1·05	0·93	0·47	0·71	0·96	0·67	0·45	0·52
	Lime	2·61	2·65	2·71	2·56	2·34	3·20	4·79	2·86
	Magnesia	2·08	3·18	3·23	2·51	2·45	1·24	1·67	2·00
	Potash	12·54	13·82	15·11	15·12	9·82	10·32	16·41	18·01
	Soda	0·32	0·75	0·48	0·30	0·48	0·52	0·47	0·44
	Phosphoric anhydride	3·93	2·77	4·70	4·82	3·33	4·31	2·93	3·41
	Sulphuric anhydride	1·92	2·64	3·11	3·25	2·21	2·41	4·38	2·72
	Chlorine	1·34	1·73	2·04	1·99	1·00	0·80	2·30	3·02
	Silica	68·35	64·99	68·48	58·99	70·74	49·05	59·05	75·69
	Total	94·14	93·46	100·33	90·25	93·33	72·52	92·45	108·67
	Deduct O = Cl	0·30	0·39	0·46	0·46	0·23	0·18	0·52	0·69
	Total	93·84	93·07	99·87	89·79	93·10	72·34	91·93	107·98
Total produce (grain and straw), per acre, lbs.	Fresh produce	2664	2843	2721	2710	2457	1772	3496	2859
	Dry matter	2152	2336	2260	2285	2032	1441	2931	2389
	Nitrogen	24·0	24·0	22·9	23·0	22·3	15·8	29·0	26·6
Ash-constituents of total produce (grain and straw), per acre, lbs.	Ferric oxide	1·26	1·13	0·69	0·84	1·12	0·76	0·59	0·63
	Lime	3·05	3·25	3·21	3·09	2·75	3·41	5·39	3·35
	Magnesia	3·67	5·03	4·90	4·31	4·13	1·94	4·02	3·83
	Potash	17·32	20·54	20·69	21·28	14·09	12·73	24·09	24·24
	Soda	0·42	0·83	0·64	0·38	0·57	0·56	0·63	0·53
	Phosphoric anhydride	11·80	11·85	13·12	13·52	10·78	7·41	14·02	12·74
	Sulphuric anhydride	2·04	2·99	3·30	3·45	2·35	2·57	4·73	2·84
	Chlorine	1·34	1·73	2·05	2·00	1·01	0·81	2·31	3·03
	Silica	68·56	65·13	68·67	59·12	70·93	49·13	59·15	75·86
	Total	109·46	112·48	117·27	107·99	107·73	79·32	114·93	127·05
	Deduct O = Cl	0·30	0·39	0·46	0·46	0·23	0·18	0·52	0·69
	Total	109·16	112·09	116·81	107·53	107·50	79·14	114·41	126·36

Straw, grown at Rothamsted, year after year on the same Land.

Fresh Produce, Dry Matter, Nitrogen, Ash-Constituents, and Total Ash duce, in sixteen consecutive Seasons, 1848–1863.

Plot 3.—*Unmanured, every year.*

1856	1857	1858	1859	1860	1861	1862	1863	Average.	Harvests.
57·3	78·3	68·3	48·3	50·6	58·7	58·2	70·4	59·5	Grain to 100 straw.
54·3	58·3	60·4	52·5	52·6	57·4	57·8	62·7	57·4	Wt. per bushel of grain, lbs.
892	1236	1141	1051	738	736	996	1127	990	Fresh produce.
733	1049	953	866	613	626	820	946	825	Dry matter.
14·0	20·0	17·7	17·0	11·8	12·8	14·4	15·6	15·7	Nitrogen.
0·13	0·22	0·20	0·17	0·21	0·14	0·22	0·09	0·16	Ferric oxide.
0·38	0·68	0·53	0·49	0·36	0·37	0·42	0·49	0·47	Lime.
1·61	2·18	2·02	1·98	1·21	1·31	1·70	2·01	1·72	Magnesia.
4·57	6·46	6·30	5·75	4·45	4·72	5·38	5·95	5·46	Potash.
0·10	0·09	0·09	0·07	0·10	0·07	0·20	0·14	0·10	Soda.
7·85	10·09	9·79	9·11	6·29	6·51	8·25	9·49	8·28	Phosphoric anhydride.
0·16	0·26	0·13	0·23	0·29	0·23	0·27	0·12	0·21	Sulphuric anhydride.
trace	0·01	none	0·02	0·03	0·02	0·01	none	0·01	Chlorine.
0·15	0·20	0·19	0·19	0·32	0·34	0·19	0·11	0·18	Silica.
14·95	20·19	19·25	18·01	13·26	13·71	16·64	18·40	16·59	Total.
—	—	—	—	0·01	—	—	—	—	Deduct O = Cl.
14·95	20·19	19·25	18·01	13·25	13·71	16·64	18·40	16·59	Total.
1558	1577	1670	2175	1459	1254	1713	1600	1663	Fresh produce.
1312	1331	1426	1838	1248	1070	1432	1345	1390	Dry matter.
5·4	6·0	6·4	9·4	7·2	6·7	6·3	4·4	7·0	Nitrogen.
0·90	1·05	0·53	0·90	1·37	0·23	0·67	0·32	0·73	Ferric oxide.
3·54	1·86	4·82	5·95	4·26	3·14	3·70	4·20	3·45	Lime.
1·30	2·24	1·72	1·56	1·08	1·06	1·28	1·42	1·88	Magnesia.
9·13	9·67	13·67	12·84	11·99	15·15	10·78	12·47	12·93	Potash.
0·46	1·35	0·49	0·62	0·35	0·26	0·35	0·24	0·49	Soda.
3·08	2·25	2·38	3·58	3·62	2·69	3·02	3·03	3·36	Phosphoric anhydride.
2·44	1·75	3·49	3·35	2·48	2·97	2·59	2·74	2·78	Sulphuric anhydride.
1·13	1·39	2·06	1·37	1·19	2·34	1·19	1·96	1·68	Chlorine.
55·25	42·85	50·35	68·04	77·87	45·95	75·30	69·83	62·55	Silica.
77·23	64·41	79·51	98·21	104·21	73·79	98·88	96·21	89·85	Total.
0·26	0·31	0·46	0·31	0·26	0·53	0·28	0·44	0·38	Deduct O = Cl.
76·97	64·10	79·05	97·90	103·95	73·26	98·60	95·77	89·47	Total.
2450	2813	2811	3226	2197	1990	2709	2727	2653	Fresh produce.
2045	2380	2379	2704	1861	1696	2252	2291	2215	Dry matter.
19·4	26·0	24·1	26·4	19·0	19·5	20·7	20·0	22·7	Nitrogen.
1·03	1·27	0·73	1·07	1·58	0·37	0·89	0·41	0·89	Ferric oxide.
3·92	2·54	5·35	6·44	4·62	3·51	4·12	4·69	3·92	Lime.
2·91	4·42	3·74	3·54	2·29	2·37	2·98	3·43	3·60	Magnesia.
13·70	16·13	19·97	18·59	16·44	19·87	16·16	18·42	18·39	Potash.
0·56	1·44	0·58	0·69	0·45	0·33	0·55	0·38	0·59	Soda.
10·93	12·34	12·17	12·69	9·91	9·20	11·27	12·52	11·64	Phosphoric anhydride.
2·60	2·01	3·62	3·58	2·77	3·20	2·86	2·86	2·99	Sulphuric anhydride.
1·13	1·40	2·06	1·39	1·22	2·36	1·20	1·96	1·69	Chlorine.
55·40	43·05	50·54	68·23	78·19	46·29	75·49	69·94	62·73	Silica.
92·18	84·60	98·76	116·22	117·47	87·50	115·52	114·61	106·44	Total.
0·26	0·31	0·46	0·31	0·27	0·53	0·28	0·44	0·38	Deduct O = Cl.
91·92	84·29	98·30	115·91	117·20	86·97	115·24	114·17	106·06	Total.

Composition of the Ash of Wheat-Grain, and of Wheat-

Appendix-Table IX.—General Characters of the Produce, and Quantities of (pure), *per Acre*, in Grain, Straw, and Total Produce,

Plot 10a.—Ammonium-Salts alone, every year.

Harvests		1848	1849	1850	1851	1852	1853	1854	1855
Grain to 100 straw		56·3	75·1	55·7	64·0	47·3	31·3	61·5	51·2
Weight per bushel of grain, lbs.		58·1	62·3	60·2	61·9	55·9	48·6	60·5	57·1
Produce of grain, per acre, lbs.	Fresh produce	1334	2141	1721	1966	1320	642	2211	1285
	Dry matter	1083	1771	1451	1661	1106	517	1877	1082
	Nitrogen	26·2	34·5	30·9	35·7	27·4	12·6	43·2	26·0
Ash-constituents of grain, per acre, lbs.	Ferric oxide	0·22	0·23	0·21	0·25	0·13	0·12	0·25	0·15
	Lime	0·68	1·02	0·98	1·05	0·71	0·38	1·09	0·74
	Magnesia	2·29	3·04	2·89	3·20	2·57	0·95	3·28	2·14
	Potash	6·48	10·51	8·96	9·79	5·69	3·66	11·54	7·14
	Soda	0·17	0·13	0·08	0·20	0·10	0·08	0·17	0·07
	Phosphoric anhydride	10·86	13·56	13·30	14·88	10·72	4·56	14·87	9·80
	Sulphuric anhydride	0·17	0·80	0·42	0·44	0·13	0·25	0·72	0·33
	Chlorine	trace	0·01	0·01	0·01	trace	0·02	0·15	0·06
	Silica	0·30	0·25	0·16	0·19	0·21	0·19	0·23	0·20
	Total	21·17	29·55	27·01	30·01	20·26	10·21	32·30	20·63
	Deduct O = Cl	—	—	—	—	—	—	0·03	0·01
	Total	21·17	29·55	27·01	30·01	20·26	10·21	32·27	20·62
Produce of straw per acre, lbs.	Fresh produce	2367	2851	3089	3070	2787	2049	3597	2512
	Dry matter	1960	2392	2647	2606	2322	1658	3032	2087
	Nitrogen	16·1	20·3	20·6	19·3	20·7	21·4	17·0	12·9
Ash-constituents of straw, per acre, lbs.	Ferric oxide	0·60	1·08	0·61	0·74	0·98	1·16	0·52	0·34
	Lime	5·54	9·76	8·68	8·41	7·27	4·76	7·84	5·46
	Magnesia	1·52	3·02	3·06	3·33	2·09	1·29	2·39	1·48
	Potash	14·50	20·63	24·44	24·07	13·68	16·40	32·22	25·80
	Soda	0·79	2·56	2·41	2·09	1·71	0·85	0·71	1·01
	Phosphoric anhydride	3·44	3·78	4·87	5·12	3·26	4·21	2·95	2·45
	Sulphuric anhydride	3·28	4·95	5·83	4·63	3·31	3·15	6·56	5·25
	Chlorine	2·03	4·60	5·25	5·82	2·01	2·44	6·96	5·30
	Silica	75·28	90·00	86·24	88·31	96·11	63·39	79·10	71·16
	Total	106·98	140·38	141·39	142·52	130·42	97·65	139·25	118·25
	Deduct O = Cl	0·46	1·04	1·17	1·32	0·46	0·55	1·57	1·19
	Total	106·52	139·34	140·22	141·20	129·96	97·10	137·68	117·06
Total produce (grain and straw), per acre, lbs.	Fresh produce	3701	4992	4810	5036	4107	2691	5808	3797
	Dry matter	3043	4163	4098	4267	3428	2175	4909	3169
	Nitrogen	42·3	54·8	51·5	55·0	48·1	34·0	60·2	38·9
Ash-constituents of total produce (grain and straw), per acre, lbs.	Ferric oxide	0·82	1·31	0·82	0·99	1·11	1·28	0·77	0·49
	Lime	6·22	10·78	9·66	9·46	7·98	5·14	8·93	6·20
	Magnesia	3·81	6·06	5·95	6·53	4·66	2·24	5·67	3·62
	Potash	20·98	31·14	33·40	33·86	19·37	20·06	43·76	32·94
	Soda	0·96	2·69	2·49	2·29	1·81	0·93	0·88	1·08
	Phosphoric anhydride	14·30	17·34	18·17	20·00	13·98	8·77	17·82	12·25
	Sulphuric anhydride	3·45	5·75	6·25	5·07	3·44	3·40	7·28	5·58
	Chlorine	2·03	4·61	5·26	5·83	2·01	2·46	7·11	5·36
	Silica	75·58	90·25	88·40	88·50	96·32	63·58	79·33	71·36
	Total	128·15	169·93	168·40	172·53	150·68	107·86	171·55	138·88
	Deduct O = Cl	0·46	1·04	1·17	1·32	0·46	0·55	1·60	1·20
	Total	127·69	168·89	167·23	171·21	150·22	107·31	169·95	137·68

grown at Rothamsted, year after year on the same Land.

Fresh Produce, Dry Matter, Nitrogen, Ash-Constituents, and Total Ash in sixteen consecutive Seasons, 1848–1863.

Plot 10*a*.—*Ammonium-Salts alone, every year.*

1856	1857	1858	1859	1860	1861	1862	1863	Average.	Harvests.
53·4	75·9	67·6	44·2	40·9	44·2	56·2	74·3	57·2	Grain to 100 straw.
55·6	58·0	59·6	51·5	49·5	55·0	56·5	62·6	57·1	Wt. per bushel of grain, lbs.
1505	1816	1439	1207	905	854	1457	2587	1524	Fresh produce.
1264	1542	1208	994	770	725	1217	2194	1279	Dry matter.
28·2	32·1	26·9	22·9	17·2	15·1	23·0	37·3	27·5	Nitrogen.
0·14	0·32	0·14	0·18	0·30	0·10	0·24	0·21	0·20	Ferric oxide.
0·84	1·11	0·93	0·67	0·56	0·51	0·80	1·32	0·84	Lime.
2·67	2·94	2·41	2·08	1·49	1·45	2·41	3·83	2·48	Magnesia.
7·44	7·96	7·68	6·05	5·68	5·16	7·66	11·78	7·70	Potash.
0·09	0·10	0·09	0·14	0·10	0·07	0·21	0·19	0·12	Soda.
11·69	11·84	10·69	8·73	7·07	6·48	9·94	15·76	10·02	Phosphoric anhydride.
0·23	0·53	0·63	0·44	0·58	0·38	0·65	0·81	0·47	Sulphuric anhydride.
none	0·03	0·13	0·01	0·14	0·17	0·15	0·07	0·06	Chlorine.
0·26	0·38	0·23	0·22	0·43	0·25	0·40	0·29	0·26	Silica.
23·36	25·21	22·93	18·52	16·35	14·57	22·46	34·26	23·05	Total.
—	0·01	0·03	—	0·03	0·04	0·03	0·02	0·01	Deduct O = Cl.
23·36	25·20	22·90	18·52	16·32	14·53	22·43	34·24	23·04	Total.
2818	2392	2130	2730	2213	1930	2593	3481	2663	Fresh produce.
2347	2033	1819	2327	1876	1635	2162	2930	2240	Dry matter.
11·7	11·4	11·5	14·9	10·3	11·6	12·5	10·3	15·1	Nitrogen.
0·76	0·85	0·47	0·90	1·65	0·19	0·55	0·35	0·73	Ferric oxide.
5·98	6·20	7·25	8·35	5·03	5·49	6·81	10·95	7·12	Lime.
1·30	1·52	2·05	2·02	1·71	1·86	2·42	2·75	2·11	Magnesia.
15·00	14·17	14·55	13·25	23·31	21·65	16·09	22·57	19·52	Potash.
1·84	0·65	0·97	1·88	0·19	1·77	1·20	0·83	1·34	Soda.
3·58	2·42	2·64	3·54	6·50	2·83	3·95	2·73	3·65	Phosphoric anhydride.
4·28	3·43	6·55	4·53	4·49	4·76	4·06	6·13	4·70	Sulphuric anhydride.
1·71	2·21	2·38	1·77	2·34	3·74	1·99	5·62	3·51	Chlorine.
73·39	49·89	47·60	63·88	106·95	56·12	81·27	107·67	77·27	Silica.
107·84	81·44	84·46	100·12	152·17	98·41	118·32	159·60	119·95	Total.
0·39	0·50	0·54	0·40	0·53	0·84	0·45	1·27	0·79	Deduct O = Cl.
107·45	80·94	83·92	99·72	151·64	97·57	117·87	158·33	119·16	Total.
4323	4208	3569	3937	3118	2784	4050	6068	4187	Fresh produce.
3611	3575	3027	3321	2646	2360	3379	5124	3519	Dry matter.
39·9	43·5	38·4	37·8	27·5	26·7	35·5	47·6	42·6	Nitrogen.
0·90	1·17	0·61	1·08	1·95	0·29	0·77	0·56	0·93	Ferric oxide.
6·82	7·41	8·18	9·02	5·59	6·00	7·61	12·27	7·96	Lime.
3·97	4·46	4·46	4·10	3·20	3·31	4·83	6·58	4·59	Magnesia.
22·44	22·13	22·23	19·30	28·99	26·81	23·75	34·35	27·22	Potash.
1·93	0·75	1·06	2·02	0·29	1·84	1·41	1·02	1·46	Soda.
15·27	14·26	13·33	12·27	13·57	9·31	13·89	18·49	14·57	Phosphoric anhydride.
4·51	3·96	7·18	4·97	5·07	5·14	4·71	6·94	5·17	Sulphuric anhydride.
1·71	2·24	2·51	1·78	2·48	3·91	2·14	5·69	3·57	Chlorine.
73·65	50·27	47·83	64·10	107·38	56·37	81·67	107·96	77·53	Silica.
131·20	106·65	107·39	118·64	168·52	112·98	140·78	193·86	143·00	Total.
0·39	0·51	0·57	0·40	0·56	0·88	0·48	1·29	0·80	Deduct O = Cl.
130·81	106·14	106·82	118·24	167·96	112·10	140·30	192·57	142·20	Total.

Appendix-Table X.—General Characters of the Produce, and *Percentage Composition of the Ash* (excluding Sand and Charcoal), of

Plots and manures.	2. Farmyard manure.				3. Unmanured.				5a. Mixed mineral manure.				7a. Mix. min. man. and amm. salts.				10a. Ammonium-sal		
Harvests.	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1
Grain to 100 straw	49·6	52·8	65·5	67·5	53·9	57·3	68·3	70·4	54·5	58·0	77·5	76·1	41·9	50·7	61·8	59·4	47·3	53·4	6
Wt. per bushel of grain, lbs.	58·2	58·6	62·6	63·1	56·6	54·3	60·4	62·7	57·5	56·5	61·5	63·0	56·0	58·0	61·9	62·6	55·9	55·6	5
Composition of the																			
Dry matter	83·25	82·58	83·56	84·63	82·57	82·18	83·55	83·97	83·45	82·28	83·60	84·15	83·70	82·67	83·81	84·33	83·75	83·98	8
Nitrogen } in dry matter {	2·02	1·89	1·91	1·52	2·08	1·91	1·86	1·65	1·88	1·89	1·71	1·54	2·29	1·98	1·98	1·53	2·48	2·23	
Ash (pure) } in dry matter {	1·98	1·98	2·04	1·85	2·03	2·04	2·02	1·95	2·05	2·07	2·04	1·93	1·95	1·91	2·00	1·73	1·83	1·85	
Composition of the G																			
Ferric oxide	0·95	0·86	0·90	0·43	1·07	0·87	1·03	0·51	1·05	0·46	0·45	0·46	1·05	0·47	0·45	0·48	0·64	0·59	
Lime	2·79	2·53	2·61	2·34	2·87	2·55	2·76	2·66	3·04	2·63	3·14	2·47	3·04	2·69	2·68	2·73	3·51	3·61	
Magnesia	12·77	11·71	11·17	11·41	11·67	10·76	10·50	10·91	12·63	10·98	9·38	11·08	12·86	12·61	10·82	10·83	12·70	11·41	1
Potash	27·22	29·27	31·87	31·54	29·66	30·55	32·74	32·32	28·89	30·54	33·90	32·18	28·64	30·23	33·46	33·64	28·10	31·86	3
Soda	0·45	0·42	0·28	0·66	0·61	0·65	0·49	0·76	0·56	0·35	0·39	0·68	0·62	0·26	0·42	0·72	0·48	0·37	
Phosphoric anhydride	54·69	54·18	51·88	52·04	51·79	52·56	50·85	51·58	52·64	52·97	51·36	51·51	52·48	52·33	51·25	49·90	52·92	50·05	4
Sulphuric anhydride	0·14	0·23	0·75	0·93	0·99	1·06	0·66	0·67	0·43	0·60	0·67	0·96	0·36	0·39	0·21	1·02	0·61	1·00	
Chlorine	trace	0·07	0·06	trace	0·04	trace	none	none	trace	0·01	0·01	none	trace	0·01	0·01	trace	trace	none	
Silica	0·99	0·75	0·49	0·65	1·31	1·00	0·97	0·59	0·76	1·46	0·70	0·66	0·95	1·01	0·70	0·68	1·04	1·11	
Total	100·00	100·02	100·01	100·00	100·01	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	10
Deduct O = Cl	—	0·02	0·01	—	0·01	—	—	—	—	—	—	—	—	—	—	—	—	—	
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	10
Composition of the S																			
Dry matter	82·16	83·08	85·24	84·44	82·84	84·17	85·42	84·07	82·32	83·26	85·94	83·57	83·90	84·00	85·36	81·80	83·28	83·34	8
Nitrogen } in dry matter {	0·46	0·38	0·47	0·25	0·57	0·41	0·45	0·33	0·51	0·48	0·43	0·33	0·87	0·43	0·46	0·36	0·89	0·50	
Ash (pure) } in dry matter {	7·04	6·57	6·42	6·42	7·04	5·87	5·54	7·12	6·68	6·59	6·34	7·76	5·55	5·48	5·73	5·22	5·60	4·58	
Composition of the Str																			
Ferric oxide	0·85	0·49	0·44	0·18	1·03	1·16	0·67	0·34	1·07	1·07	0·48	0·38	1·05	1·14	0·42	0·36	0·75	0·71	
Lime	3·87	3·98	4·03	3·78	2·52	4·61	6·10	4·39	4·78	3·54	3·47	2·25	5·26	4·90	4·88	5·55	5·60	5·57	
Magnesia	1·52	1·57	1·69	1·41	2·64	1·70	2·18	1·48	1·63	1·08	1·13	1·46	1·76	1·06	1·27	1·58	1·61	1·21	
Potash	12·86	14·62	21·70	17·97	10·54	11·87	17·29	13·02	12·41	11·32	18·07	15·35	15·12	16·13	21·99	24·96	10·53	13·95	1
Soda	0·60	0·53	0·49	none	0·52	0·59	0·62	0·26	0·35	2·73	1·64	0·18	0·56	1·17	1·19	0·13	1·31	1·71	
Phosphoric anhydride	3·21	3·42	3·41	3·16	3·56	4·00	3·01	3·16	4·01	4·64	3·57	3·70	3·73	3·51	2·97	2·78	2·50	3·33	
Sulphuric anhydride	2·58	2·62	3·57	2·54	2·37	3·16	4·41	2·87	2·81	3·51	4·72	5·01	2·90	3·23	4·60	3·76	2·56	3·98	
Chlorine	1·86	2·29	4·81	3·61	1·08	1·46	2·61	2·04	1·61	1·23	2·76	1·87	2·37	2·18	6·37	6·82	1·54	1·59	
Silica	73·07	71·00	60·95	68·16	75·98	71·78	63·70	72·90	71·69	71·16	64·78	69·22	67·78	67·17	57·74	55·61	73·96	68·31	5
Total	100·42	100·52	101·09	100·81	100·24	100·33	100·59	100·46	100·36	100·28	100·62	100·42	100·53	100·49	101·43	101·55	100·36	100·36	10
Deduct O = Cl	0·42	0·52	1·09	0·81	0·24	0·33	0·59	0·46	0·36	0·28	0·62	0·42	0·53	0·49	1·43	1·55	0·36	0·36	
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	10

t-Straw, grown at Rothamsted, year after year on the same Land.

oal), of the Grain, and of the Straw, from nine differently manured Plots, in four characteristic Seasons—1852, 1856, 1858, and 1863.

10a. monium-salts alone.			11a. Amm. salts and superphosphate.				12a. Amm., superph., and soda.				13a. Amm., superph., and potash.				14a. Amm., superph., and magnesia.				Plots and manures.
1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	Harvests.
53·4	67·6	74·3	47·8	56·9	70·7	70·4	46·1	54·7	66·5	64·9	45·9	54·4	64·6	60·2	42·5	52·2	64·6	64·6	Grain to 100 straw.
55·6	59·6	62·6	55·6	57·3	60·5	62·5	57·4	58·7	62·1	62·1	57·5	58·6	62·1	62·6	56·9	58·6	62·1	62·5	Wt. per bushel of grain, lbs.
of the Grain, per cent.																			
83·98	83·92	84·80	83·95	83·65	83·88	84·73	83·37	83·11	83·82	85·24	83·57	84·27	83·67	84·11	83·50	84·02	84·00	84·56	Dry matter.
2·23	2·23	1·70	1·95	2·00	2·01	1·79	1·77	1·91	1·92	1·74	1·80	2·00	2·00	1·68	1·87	2·02	1·95	1·72	Nitrogen } in dry matter.
1·85	1·90	1·56	1·96	1·92	1·89	1·72	1·96	1·91	1·92	1·75	1·95	1·87	1·94	1·75	1·95	1·88	1·95	1·74	Ash (pure) }
f the Grain-Ash, per cent.																			
0·59	0·63	0·59	0·97	1·24	1·00	0·57	0·82	1·11	1·12	0·48	0·81	1·24	0·85	0·57	0·92	1·12	0·75	0·46	Ferric oxide.
3·61	4·05	3·85	3·80	3·82	3·82	3·89	3·13	2·94	3·04	3·35	3·08	2·86	2·98	2·75	3·27	2·66	2·82	3·01	Lime.
11·41	10·52	11·20	13·19	11·01	9·96	10·71	12·73	10·96	10·21	10·50	12·81	10·82	10·28	10·63	12·82	11·07	10·47	11·15	Magnesia.
31·86	33·52	34·42	27·19	28·58	32·93	32·58	28·42	29·98	33·70	33·78	28·75	30·14	33·66	34·39	28·51	29·43	32·94	33·38	Potash.
0·37	0·37	0·54	0·56	0·34	0·52	0·55	0·57	0·29	0·38	0·43	0·62	0·29	0·15	0·33	0·77	0·32	0·58	0·60	Soda.
50·05	46·69	46·02	53·18	53·01	49·09	49·74	52·85	53·63	49·96	48·97	52·87	53·26	50·44	49·56	52·84	53·23	51·11	49·47	Phosphoric anhydride.
1·00	2·78	2·37	0·18	0·94	1·68	1·26	0·54	0·25	1·04	1·75	0·31	0·60	0·89	1·11	0·23	1·06	0·82	1·30	Sulphuric anhydride.
none	0·55	0·19	trace	0·05	0·06	trace	trace	0·03	trace	0·18	trace	0·03	0·05	trace	none	0·06	0·02	0·11	Chlorine.
1·11	1·01	0·86	0·93	1·02	0·95	0·70	0·94	0·82	0·53	0·60	0·75	0·77	0·71	0·66	0·64	1·06	0·49	0·54	Silica.
100·00	100·12	100·04	100·00	100·01	100·01	100·00	100·00	100·01	100·00	100·04	100·00	100·01	100·01	100·00	100·00	100·01	100·00	100·02	Total.
—	0·12	0·04	—	0·01	0·01	—	—	0·01	—	0·04	—	0·01	0·01	—	—	0·01	—	0·02	Deduct O = Cl.
100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	Total.
of the Straw, per cent.																			
83·34	85·36	84·17	83·00	83·92	85·39	83·59	83·87	83·33	84·08	83·30	83·04	83·60	83·76	82·70	83·44	83·66	84·88	83·11	Dry matter.
0·50	0·63	0·35	0·46	0·43	0·52	0·44	0·47	0·33	0·40	0·37	0·49	0·29	0·40	0·25	0·55	0·36	0·41	0·27	Nitrogen } in dry matter.
4·58	4·61	5·40	6·10	4·75	5·32	5·48	6·06	4·53	5·21	5·33	5·83	5·14	5·64	5·31	5·79	4·56	5·35	5·36	Ash (pure) }
f the Straw-Ash, per cent.																			
0·71	0·55	0·22	1·05	1·02	0·61	0·60	0·98	0·69	0·54	0·33	0·87	1·28	0·48	0·28	0·82	0·42	0·56	0·34	Ferric oxide.
5·57	8·64	6·92	5·78	6·34	6·91	7·39	5·10	5·53	6·20	6·80	4·93	4·43	5·04	4·93	5·32	6·12	5·61	6·31	Lime.
1·21	2·44	1·74	1·66	1·61	1·81	2·21	1·58	1·56	1·60	1·99	1·52	1·37	1·29	1·56	1·55	1·88	1·97	2·01	Magnesia.
13·95	17·34	14·25	5·12	9·04	13·19	9·31	13·22	16·41	20·75	17·35	14·17	18·34	26·89	23·17	14·18	20·37	21·37	19·06	Potash.
1·71	1·16	0·52	1·23	1·21	1·55	1·63	0·61	0·85	0·63	1·09	0·56	0·38	0·24	0·58	0·64	0·46	0·40	0·86	Soda.
3·33	3·15	1·73	3·21	3·14	3·18	2·81	3·36	3·01	2·87	1·87	3·46	2·83	2·69	1·94	3·46	3·46	2·83	1·82	Phosphoric anhydride.
3·98	7·79	3·88	1·62	2·97	5·15	3·67	2·30	3·21	5·03	3·30	2·29	3·03	5·06	2·97	2·56	3·30	4·96	3·25	Sulphuric anhydride.
1·59	2·85	3·55	0·66	1·39	2·56	2·97	1·94	2·96	5·06	4·19	2·12	3·31	7·33	5·58	2·09	3·38	5·18	4·84	Chlorine.
68·31	56·73	67·99	79·82	73·59	65·62	70·07	71·35	66·45	58·45	64·03	70·56	65·78	52·64	60·26	69·86	61·38	58·29	62·60	Silica.
100·36	100·65	100·80	100·15	100·31	100·58	100·66	100·44	100·67	101·13	100·95	100·48	100·75	101·66	101·27	100·48	100·77	101·17	101·09	Total.
0·36	0·65	0·80	0·15	0·31	0·58	0·66	0·44	0·67	1·13	0·95	0·48	0·75	1·66	1·27	0·48	0·77	1·17	1·09	Deduct O = Cl.
100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	Total.

Appendix-Table XI.—General Characters of the Produce, and Amounts of Nitrogen, Ash-Constituents, and Total Ash (pure), *per* 1000
Seasons—1852, 1856, 185

Plots and manures.	2. Farmyard manure.				3. Unmanured.				5a. Mixed mineral manure.				7a. Mix. min. man. and amm. salts.				10a. Ammonium-salts alone			
Harvests.	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	
Grain to 100 straw	49·6	52·8	65·5	67·5	53·9	57·3	68·3	70·4	54·5	58·0	77·5	76·1	41·9	50·7	61·8	59·4	47·3	53·4	67·6	
Wt. per bushel of grain, lbs.	58·2	58·6	62·6	63·1	56·6	54·3	60·4	62·7	57·5	56·5	61·5	63·0	56·0	58·0	61·9	62·6	55·9	55·6	59·9	
Per* 1000 *Dry Matter o																				
Fresh produce	1201	1211	1197	1182	1211	1217	1197	1191	1197	1216	1197	1188	1195	1210	1193	1186	1193	1191	1191	11
Nitrogen	20·2	18·9	19·1	15·2	20·8	19·1	18·6	16·5	18·8	18·9	17·1	15·4	22·9	19·8	19·8	15·3	24·8	22·3	22·3	
Ash-Constituents*, *per* 1000 *Dry																				
Ferric oxide	0·19	0·17	0·19	0·08	0·22	0·18	0·21	0·10	0·21	0·10	0·09	0·09	0·21	0·09	0·09	0·08	0·12	0·11	0·12	
Lime	0·55	0·50	0·53	0·43	0·58	0·52	0·56	0·52	0·62	0·54	0·64	0·48	0·60	0·52	0·54	0·47	0·64	0·67	0·77	
Magnesia	2·53	2·32	2·28	2·12	2·36	2·19	2·12	2·12	2·59	2·28	1·92	2·13	2·51	2·41	2·16	1·88	2·33	2·11	1·99	
Potash	5·38	5·80	6·52	5·85	6·01	6·23	6·61	6·28	5·91	6·33	6·93	6·19	5·59	5·78	6·68	5·83	5·15	5·88	6·35	
Soda	0·09	0·08	0·06	0·12	0·13	0·13	0·10	0·15	0·12	0·07	0·08	0·13	0·12	0·05	0·08	0·12	0·09	0·07	0·07	
Phosphoric anhydride	10·83	10·73	10·61	9·65	10·50	10·72	10·27	10·03	10·78	10·97	10·49	9·92	10·24	10·00	10·24	8·65	9·69	9·25	8·85	
Sulphuric anhydride	0·03	0·05	0·15	0·17	0·20	0·22	0·13	0·13	0·09	0·13	0·14	0·18	0·07	0·07	0·04	0·18	0·11	0·19	0·53	
Chlorine	trace	0·01	0·01	none	0·01	trace	none	none	trace	trace	trace	none	trace	trace	trace	trace	trace	none	0·11	
Silica	0·20	0·15	0·10	0·12	0·27	0·20	0·20	0·12	0·16	0·30	0·14	0·13	0·19	0·19	0·14	0·12	0·19	0·20	0·19	
Total	19·80	19·81	20·45	18·54	20·28	20·39	20·20	19·45	20·48	20·72	20·43	19·25	19·53	19·11	19·97	17·33	18·32	18·48	18·98	
Deduct O = Cl	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0·02	
Total	19·80	19·81	20·45	18·54	20·28	20·39	20·20	19·45	20·48	20·72	20·43	19·25	19·53	19·11	19·97	17·33	18·32	18·48	18·96	
Per* 1000 *Dry Matter of																				
Fresh produce	1216	1204	1174	1184	1194	1188	1171	1190	1215	1200	1164	1196	1192	1191	1171	1222	1200	1201	1171	11
Nitrogen	4·6	3·8	4·7	2·5	5·7	4·1	4·5	3·3	5·1	4·8	4·3	3·3	8·7	4·3	4·6	3·6	8·9	5·0	6·3	
Ash-Constituents*, *per* 1000 *Dry																				
Ferric oxide	0·59	0·32	0·28	0·12	0·73	0·69	0·37	0·24	0·72	0·71	0·31	0·30	0·58	0·62	0·24	0·19	0·42	0·32	0·26	
Lime	2·73	2·61	2·59	2·43	1·77	2·70	3·38	3·13	3·19	2·33	2·20	2·52	2·92	2·68	2·79	2·89	3·13	2·55	3·98	
Magnesia	1·07	1·03	1·09	0·91	1·85	0·99	1·21	1·06	1·09	0·71	0·72	1·14	0·98	0·58	0·73	0·82	0·90	0·55	1·13	
Potash	9·06	9·60	13·92	11·53	7·43	6·96	9·59	9·27	8·28	7·46	11·45	11·91	8·39	8·84	12·61	13·03	5·89	6·39	8·00	
Soda	0·42	0·35	0·31	none	0·36	0·35	0·34	0·18	0·23	1·80	1·04	0·14	0·31	0·64	0·68	0·07	0·74	0·79	0·54	
Phosphoric anhydride	2·27	2·25	2·19	2·02	2·52	2·35	1·67	2·25	2·68	3·06	2·26	2·87	2·07	1·93	1·70	1·45	1·40	1·53	1·45	
Sulphuric anhydride	1·82	1·72	2·28	1·63	1·67	1·86	2·45	2·03	1·88	2·31	2·99	3·88	1·61	1·77	2·63	1·96	1·43	1·82	3·60	
Chlorine	1·31	1·50	3·09	2·32	0·76	0·86	1·44	1·45	1·08	0·81	1·75	1·45	1·31	1·20	3·65	3·56	0·97	0·73	1·31	
Silica	51·47	46·64	39·10	43·74	53·51	42·11	35·31	51·92	47·85	46·88	41·04	53·69	37·61	36·81	33·10	29·02	41·39	31·27	26·16	
Total	70·74	66·02	64·85	64·70	70·60	58·87	55·76	71·53	67·00	66·07	63·76	77·80	55·78	55·07	58·13	52·99	56·17	45·95	46·43	
Deduct O = Cl	0·30	0·34	0·69	0·52	0·17	0·20	0·33	0·33	0·25	0·19	0·39	0·33	0·30	0·27	0·82	0·81	0·20	0·16	0·30	
Total	70·44	65·68	64·16	64·18	70·43	58·67	55·43	71·20	66·75	65·88	63·37	77·57	55·48	54·80	57·31	52·18	55·97	45·79	46·13	
Per* 1000 *Dry Matter of Total Produc																				
Fresh produce	1211	1206	1183	1183	1209	1198	1182	1190	1209	1206	1178	1193	1193	1197	1179	1209	1198	1197	1179	118
Nitrogen	9·8	9·0	10·3	7·6	11·0	9·5	10·1	8·7	10·0	9·9	9·8	8·6	12·9	9·5	10·3	8·0	14·0	11·0	12·7	
Ash-Constituents, per* 1000 *Dry Matter of Tota																				
Ferric oxide	0·46	0·27	0·24	0·10	0·55	0·51	0·31	0·18	0·54	0·48	0·22	0·21	0·47	0·45	0·18	0·15	0·32	0·25	0·20	
Lime	2·00	1·89	1·78	1·63	1·36	1·92	2·25	2·05	2·27	1·68	1·53	1·63	2·23	1·96	1·94	1·98	2·33	1·89	2·70	
Magnesia	1·56	1·48	1·56	1·39	2·03	1·42	1·57	1·50	1·63	1·28	1·23	1·57	1·43	1·19	1·27	1·22	1·36	1·10	1·47	
Potash	7·83	8·29	11·03	9·24	6·93	6·70	8·40	8·04	7·44	7·05	9·51	9·43	7·56	7·82	10·37	10·29	5·65	6·21	7·35	
Soda	0·31	0·26	0·21	0·05	0·28	0·27	0·24	0·17	0·19	1·17	0·63	0·14	0·26	0·44	0·46	0·09	0·53	0·53	0·35	
Phosphoric anhydride	5·13	5·17	5·48	5·10	5·31	5·35	5·12	5·46	5·56	5·94	5·80	5·92	4·48	4·61	4·92	4·18	4·08	4·23	4·41	
Sulphuric anhydride	1·22	1·14	1·45	1·04	1·16	1·27	1·52	1·25	1·24	1·52	1·76	2·28	1·15	1·21	1·66	1·29	1·00	1·25	2·37	
Chlorine	0·87	0·99	1·88	1·38	0·50	0·55	0·87	0·85	0·69	0·52	1·00	0·82	0·93	0·80	2·27	2·21	0·59	0·47	0·83	
Silica	34·31	30·64	23·86	26·15	34·90	27·09	21·24	30·53	30·86	29·91	23·46	30·46	26·57	24·62	20·66	18·04	28·10	20·40	15·80	2
Total	53·69	50·13	47·49	46·08	53·02	45·08	41·52	50·03	50·42	49·55	45·14	52·46	45·08	43·10	43·73	39·44	43·96	36·33	35·48	3
Deduct O = Cl	0·20	0·23	0·42	0·31	0·11	0·13	0·20	0·19	0·16	0·12	0·23	0·19	0·21	0·18	0·51	0·50	0·14	0·11	0·19	
Total	53·49	49·90	47·07	45·77	52·91	44·95	41·32	49·84	50·26	49·43	44·91	52·27	44·87	42·92	43·22	38·94	43·82	36·22	35·29	3

aw, grown at Rothamsted, year after year on the same Land.

per 1000 *Dry Matter* (at 100° C.), of Grain, Straw, and Total Produce, from nine differently manured Plots, in four characteristic 56, 1858, and 1863.

10a. -salts alone.		11a. Amm. salts and superphosphate.				12a. Amm., superph., and soda.				13a. Amm., superph., and potash.				14a. Amm., superph., and magnesia.				Plots and manures.
1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	Harvests.
67·6	74·3	47·8	56·9	70·7	70·4	46·1	54·7	66·5	64·9	45·9	54·4	64·6	60·2	42·5	52·2	64·6	64·6	Grain to 100 straw.
59·9	62·6	55·6	57·3	60·5	62·5	57·4	58·7	62·1	62·1	57·5	58·6	62·1	62·6	56·9	58·6	62·1	62·5	Wt. per bushel of grain, lbs.
Matter of Grain.																		
1191	1179	1191	1195	1192	1180	1199	1203	1193	1173	1196	1186	1195	1189	1198	1190	1190	1183	Fresh produce.
22·3	17·0	19·5	20·0	20·1	17·9	17·7	19·1	19·2	17·4	18·0	20·0	20·0	16·8	18·7	20·2	19·5	17·2	Nitrogen.
00 Dry Matter of Grain.																		
0·12	0·09	0·19	0·24	0·19	0·10	0·16	0·21	0·22	0·08	0·16	0·23	0·16	0·10	0·16	0·21	0·15	0·08	Ferric oxide.
0·77	0·60	0·74	0·73	0·72	0·67	0·61	0·56	0·58	0·59	0·60	0·54	0·58	0·48	0·64	0·50	0·55	0·52	Lime.
1·99	1·75	2·58	2·11	1·89	1·84	2·49	2·09	1·96	1·84	2·50	2·02	2·00	1·96	2·50	2·07	2·04	1·94	Magnesia.
6·35	5·37	5·33	5·48	6·24	5·62	5·56	5·71	6·47	5·92	5·62	5·64	6·54	6·03	5·57	5·52	6·41	5·80	Potash.
0·07	0·09	0·11	0·07	0·10	0·09	0·11	0·05	0·07	0·08	0·12	0·06	0·03	0·06	0·15	0·06	0·11	0·10	Soda.
8·85	7·18	10·42	10·16	9·30	8·58	10·34	10·22	9·59	8·58	10·33	9·97	9·81	8·69	10·31	9·99	9·95	8·60	Phosphoric anhydride.
0·53	0·37	0·04	0·18	0·32	0·22	0·11	0·05	0·20	0·31	0·06	0·11	0·17	0·20	0·05	0·20	0·16	0·23	Sulphuric anhydride.
0·11	0·03	trace	0·01	0·01	trace	trace	0·01	trace	0·03	trace	0·01	0·01	trace	trace	0·01	trace	0·02	Chlorine.
0·19	0·13	0·18	0·20	0·18	0·12	0·18	0·15	0·10	0·11	0·15	0·14	0·14	0·12	0·13	0·20	0·10	0·09	Silica.
18·98	15·61	19·59	19·18	18·95	17·24	19·56	19·06	19·19	17·54	19·54	18·72	19·44	17·54	19·53	18·76	19·47	17·38	Total.
0·02	0·01	—	—	—	—	—	—	—	0·01	—	—	—	—	—	—	—	—	Deduct O = Cl.
18·96	15·60	19·59	19·18	18·95	17·24	19·56	19·06	19·19	17·53	19·54	18·72	19·44	17·54	19·53	18·76	19·47	17·38	Total.
Matter of Straw.																		
1171	1188	1205	1192	1171	1196	1192	1200	1189	1200	1205	1196	1193	1209	1199	1195	1178	1203	Fresh produce.
6·3	3·5	4·6	4·3	5·2	4·4	4·7	3·3	4·0	3·7	4·9	2·9	4·0	2·5	5·5	3·6	4·1	2·7	Nitrogen.
00 Dry Matter of Straw.																		
0·26	0·12	0·65	0·49	0·32	0·33	0·60	0·31	0·28	0·17	0·51	0·66	0·27	0·15	0·47	0·19	0·30	0·18	Ferric oxide.
3·98	3·74	3·52	3·01	3·67	4·05	3·08	2·50	3·23	3·63	2·87	2·26	2·84	2·62	3·08	2·79	3·00	3·38	Lime.
1·13	0·94	1·02	0·76	0·97	1·22	0·96	0·71	0·83	1·06	0·89	0·71	0·73	0·83	0·90	0·86	1·06	1·07	Magnesia.
8·00	7·70	3·12	4·29	7·03	5·10	8·01	7·43	10·82	9·26	8·25	9·44	15·17	12·30	8·21	9·28	11·43	10·21	Potash.
0·54	0·29	0·75	0·58	0·82	0·90	0·37	0·38	0·33	0·58	0·32	0·20	0·14	0·31	0·38	0·21	0·22	0·46	Soda.
1·45	0·93	1·96	1·49	1·69	1·53	2·04	1·36	1·50	1·00	2·02	1·45	1·52	1·03	2·00	1·58	1·51	0·98	Phosphoric anhydride.
3·60	2·09	0·99	1·41	2·75	2·02	1·40	1·45	2·62	1·76	1·34	1·56	2·85	1·58	1·48	1·50	2·66	1·75	Sulphuric anhydride.
1·31	1·92	0·40	0·66	1·36	1·62	1·17	1·34	2·64	2·24	1·24	1·70	4·13	2·96	1·20	1·54	2·77	2·60	Chlorine.
26·16	36·74	48·69	34·93	34·93	38·38	43·22	30·08	30·46	34·15	41·11	33·83	29·69	32·00	40·44	27·96	31·20	33·55	Silica.
46·43	54·47	61·10	47·62	53·54	55·15	60·85	45·56	52·71	53·85	58·55	51·81	57·34	53·78	58·16	45·91	54·15	54·18	Total.
0·30	0·43	0·09	0·15	0·31	0·36	0·27	0·31	0·60	0·50	0·28	0·39	0·93	0·67	0·27	0·35	0·63	0·59	Deduct O = Cl.
46·13	54·04	61·01	47·47	53·23	54·79	60·58	45·25	52·11	53·35	58·27	51·42	56·41	53·11	57·89	45·56	53·52	53·59	Total.
l Produce (Grain and Straw).																		
179	1184	1200	1193	1180	1190	1194	1201	1190	1190	1202	1193	1194	1202	1199	1193	1183	1195	Fresh produce.
12·7	9·3	9·5	10·0	11·3	10·0	8·8	8 9	10·1	9·2	9·1	9·7	10·3	7·9	9·4	9·3	10·1	8·4	Nitrogen.
of Total Produce (Grain and Straw).																		
0·20	0·11	0·50	0·40	0·27	0·23	0·46	0·28	0·26	0·14	0·40	0·51	0·23	0·13	0·39	0·20	0·24	0·14	Ferric oxide.
2·70	2·40	2·62	2·19	2·47	2·64	2·31	1·82	2·18	2·42	2·15	1·65	1·95	1·81	2·35	2·00	2·05	2·25	Lime.
1·47	1·28	1·53	1·25	1·34	1·48	1·44	1·20	1·28	1·37	1·40	1·17	1·22	1·22	1·38	1·28	1·44	1·42	Magnesia.
7·35	6·70	3·84	4·72	6·70	5·32	7·24	6·82	9·08	7·92	7·42	8·09	11·79	9·92	7·42	7·99	9·48	8·46	Potash.
0·25	0·20	0·54	0·39	0·53	0·56	0·29	0·27	0·22	0·38	0·26	0·15	0·10	0·21	0·31	0·16	0·18	0·32	Soda.
4·41	3·61	4·71	4·63	4·81	4·47	4·65	4·48	4·72	4·03	4·65	4·47	4·77	3·94	4·48	4·47	4 80	4·00	Phosphoric anhydride.
2·37	1·35	0·68	0·96	1·75	1·27	0·99	0·96	1·66	1·18	0·93	1·05	1·80	1·05	1·05	1·05	1·68	1·14	Sulphuric anhydride.
0·83	1·11	0·27	0·42	0·81	0·95	0·80	0·87	1·59	1·36	0·84	1·10	2·52	1·84	0·85	1·01	1·69	1·57	Chlorine.
15·80	21·07	32·88	22·36	20·69	22·45	29·68	19·52	18·35	20·56	28·16	21·90	18·11	19·90	28·40	18·41	19·07	20·28	Silica.
35·48	37·83	47·57	37·32	39·37	39·37	47·86	36·22	39·34	39·36	46·21	40·09	42·49	40·02	46·63	36·57	40·63	39·58	Total.
0·19	0·25	0·06	0·09	0·18	0·21	0·18	0·20	0·36	0·31	0·19	0·25	0·57	0·41	0·19	0·23	0·38	0·35	Deduct O = Cl.
35·29	37·58	47·51	37·23	39·19	39·16	47·68	36·02	38·98	39·05	46·02	39·84	41·92	39·61	46·44	36·34	40·25	39·23	Total.

Appendix-Table XII.—General Characters of the Produce, and Quantities of Fresh Produce, Dry Matter, Nitrogen, Ash-Consti
characteristic Seasons—1852, 18

Plots and manures.	2. Farmyard manure.				3. Unmanured.				5a. Mixed mineral manure.				7a. Mix. min. man. and amm. salts.				10a. Ammonium-salts		
Harvests.	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	185
Grain to 100 straw	49·6	52·8	65·5	67·5	53·9	57·3	68·3	70·4	54·5	58·0	77·5	76·1	41·9	50·7	61·8	59·4	47·3	53·4	67·
Wt. per bushel of grain, lbs.	58·2	58·6	62·6	63·1	56·6	54·3	60·4	62·7	57·5	56·5	61·5	63·0	56·0	58·0	61·9	62·6	55·9	55·6	59·
Produce of Grain, per																			
Fresh produce	1716	2277	2512	2886	860	892	1141	1127	1038	1167	1187	1283	1615	2312	2450	3477	1320	1505	1439
Dry matter	1429	1881	2099	2442	710	733	953	946	867	960	992	1080	1352	1911	2053	2932	1106	1264	1208
Nitrogen	28·9	35·6	40·1	37·1	14·6	14·0	17·7	15·6	16·3	18·1	17·0	16·6	31·0	37·8	40·6	44·9	27·4	28·2	26·
Ash-Constituents of Grain,																			
Ferric oxide	0·27	0·32	0·39	0·20	0·16	0·13	0·20	0·09	0·18	0·09	0·09	0·10	0·28	0·17	0·18	0·25	0·13	0·14	0·1
Lime	0·79	0·94	1·12	1·06	0·41	0·38	0·53	0·49	0·54	0·52	0·64	0·51	0·80	0·99	1·10	1·39	0·71	0·84	0·9
Magnesia	3·61	4·36	4·79	5·17	1·68	1·61	2·02	2·01	2·24	2·18	1·90	2·30	3·39	4·61	4·44	5·50	2·57	2·67	2·4
Potash	7·70	10·91	13·68	14·28	4·27	4·57	6·30	5·95	5·13	6·08	6·87	6·69	7·56	11·04	13·72	17·09	5·69	7·44	7·6
Soda	0·13	0·16	0·12	0·30	0·09	0·10	0·09	0·14	0·10	0·07	0·08	0·14	0·16	0·10	0·17	0·37	0·10	0·09	0·0
Phosphoric anhydride	15·47	20·19	22·27	23·55	7·45	7·85	9·79	9·49	9·34	10·54	10·41	10·71	13·86	19·11	21·02	25·35	10·72	11·69	10·6
Sulphuric anhydride	0·04	0·09	0·32	0·42	0·14	0·16	0·13	0·12	0·08	0·12	0·14	0·20	0·10	0·14	0·09	0·52	0·13	0·23	0·6
Chlorine	trace	0·03	0·03	none	0·01	trace	none	none	trace	trace	trace	none	trace	trace	trace	trace	trace	none	0·1
Silica	0·28	0·28	0·21	0·29	0·19	0·15	0·19	0·11	0·14	0·29	0·14	0·14	0·25	0·37	0·29	0·34	0·21	0·26	0·2
Total	28·29	37·28	42·93	45·27	14·40	14·95	19·25	18·40	17·75	19·89	20·27	20·79	26·40	36·53	41·01	50·81	20·26	23·36	22·9
Deduct O = Cl	—	0·01	0·01	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0·0
Total	28·29	37·27	42·92	45·27	14·40	14·95	19·25	18·40	17·75	19·89	20·27	20·79	26·40	36·53	41·01	50·81	20·26	23·36	22·9
Produce of Straw, per																			
Fresh produce	3457	4317	3837	4279	1597	1558	1670	1600	1903	2012	1532	1687	3850	4560	3965	5853	2787	2818	2130
Dry matter	2842	3587	3269	3613	1322	1312	1426	1345	1566	1676	1316	1410	3230	3830	3386	4788	2322	2347	1819
Nitrogen	13·1	13·6	15·4	9·0	7·5	5·4	6·4	4·4	8·0	8·0	5·7	4·7	28·1	16·5	15·6	17·2	20·7	11·7	11·5
Ash-Constituents of Straw,																			
Ferric oxide	1·09	1·15	0·92	0·42	0·96	0·90	0·53	0·32	1·12	1·19	0·41	0·42	1·88	2·39	0·81	0·89	0·98	0·76	0·4
Lime	7·76	9·38	8·46	8·77	2·34	3·54	4·82	4·20	5·00	3·91	2·89	3·56	9·43	10·27	9·46	13·85	7·27	5·98	7·2
Magnesia	3·04	3·71	3·55	3·27	2·45	1·30	1·72	1·42	1·71	1·18	0·95	1·60	3·16	2·24	2·26	3·95	2·09	1·30	2·0
Potash	25·76	34·44	45·50	41·68	9·62	9·13	13·67	12·47	12·97	12·50	15·07	16·79	27·09	33·85	42·68	62·36	13·68	15·00	14·5
Soda	1·19	1·25	1·03	none	0·48	0·46	0·49	0·24	0·36	3·02	1·37	0·20	1·01	2·45	2·31	0·33	1·71	1·84	0·9
Phosphoric anhydride	6·44	8·06	7·15	7·32	3·33	3·08	2·38	3·03	4·19	5·12	2·98	4·04	6·68	7·37	5·76	6·94	3·26	3·58	2·6
Sulphuric anhydride	5·16	6·16	7·47	5·88	2·21	2·44	3·49	2·74	2·94	3·88	3·93	5·48	5·19	6·79	8·92	9·40	3·31	4·28	6·5
Chlorine	3·72	5·38	10·08	8·37	1·00	1·13	2·06	1·96	1·69	1·36	2·30	2·04	4·24	4·58	12·36	17·03	2·01	1·71	2·3
Silica	146·27	167·29	127·84	158·03	70·74	55·25	50·35	69·83	74·94	78·57	54·01	75·70	121·49	140·97	112·07	138·94	96·11	73·39	47·6
Total	201·03	236·82	212·00	233·74	93·33	77·23	79·51	96·21	104·92	110·73	83·91	109·83	180·17	210·91	196·83	253·69	130·42	107·84	84·4
Deduct O = Cl	0·84	1·23	2·27	1·88	0·23	0·26	0·46	0·44	0·38	0·31	0·52	0·46	0·96	1·03	2·76	3·87	0·46	0·39	0·5
Total	200·19	235·59	209·73	231·86	93·10	76·97	79·05	95·77	104·54	110·42	83·39	109·37	179·21	209·88	194·07	249·82	129·96	107·45	83·9
Total Produce (Grain and Straw																			
Fresh produce	5173	6594	6349	7165	2457	2450	2811	2727	2941	3179	2719	2970	5465	6972	6415	9330	4107	4323	3569
Dry matter	4271	5468	5368	6055	2032	2045	2379	2291	2433	2636	2308	2490	4582	5741	5439	7720	3428	3611	3027
Nitrogen	42·0	49·2	55·5	46·1	22·3	19·4	24·1	20·0	24·3	26·1	22·7	21·3	59·1	54·3	56·2	62·1	48·1	39·9	38·4
Ash-Constituents of Total Produce (Gra																			
Ferric oxide	1·36	1·47	1·31	0·62	1·12	1·03	0·73	0·41	1·30	1·28	0·50	0·52	2·16	2·56	0·99	1·14	1·11	0·90	0·61
Lime	8·55	10·32	9·58	9·83	2·75	3·92	5·35	4·69	5·54	4·43	3·53	4·07	10·23	11·26	10·56	15·24	7·98	6·82	8·18
Magnesia	6·65	8·07	8·34	8·44	4·13	2·91	3·74	3·43	3·95	3·36	2·85	3·90	6·55	6·85	6·90	9·45	4·96	3·97	4·46
Potash	33·46	45·35	59·18	55·96	14·09	13·70	19·97	18·42	18·10	18·58	21·94	23·48	34·65	44·89	56·40	79·45	19·37	22·44	22·23
Soda	1·32	1·41	1·15	0·30	0·57	0·56	0·58	0·38	0·46	3·09	1·45	0·34	1·17	2·55	2·48	0·70	1·81	1·93	1·06
Phosphoric anhydride	21·91	28·25	29·42	30·87	10·78	10·93	12·17	12·52	13·53	15·66	13·39	14·75	20·54	26·48	26·78	32·29	13·98	15·27	13·33
Sulphuric anhydride	5·20	6·25	7·79	6·30	2·35	2·60	3·62	2·86	3·02	4·00	4·07	5·68	5·29	6·93	9·01	9·92	3·44	4·51	7·18
Chlorine	3·72	5·41	10·11	8·37	1·01	1·13	2·06	1·96	1·69	1·36	2·30	2·04	4·24	4·58	12·36	17·03	2·01	1·71	2·51
Silica	146·55	167·57	128·05	158·32	70·93	55·40	50·54	69·94	75·08	78·86	54·15	75·84	121·74	141·34	112·36	139·28	96·32	73·65	47·83
Total	229·32	274·10	254·93	279·01	107·72	92·18	98·76	114·61	122·67	130·62	104·18	130·62	206·57	247·44	237·84	304·50	150·68	131·20	107·39
Deduct O = Cl	0·84	1·24	2·28	1·88	0·23	0·26	0·46	0·44	0·38	0·31	0·52	0·46	0·96	1·03	2·76	3·87	0·46	0·39	0·5
Total	228·48	272·86	252·65	277·13	107·50	91·92	98·30	114·17	122·29	130·31	103·66	130·16	205·61	246·41	235·08	300·63	150·22	130·81	106·82

-Straw, grown at Rothamsted, year after year on the same Land.

n-Constituents, and Total Ash (pure), *per Acre* in Grain, Straw, and Total Produce, from nine differently manured Plots, in four 1852, 1856, 1858, and 1863.

10a. onium-salts alone.			11a. Amm. salts and superphosphate.				12a. Amm., superph., and soda.				13a. Amm., superph., and potash.				14a. Amm., superph., and magnesia.				Plots and manures.
856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	1852	1856	1858	1863	Harvests.
3·4	67·6	74·3	47·8	56·9	70·7	70·4	46·1	54·7	66·5	64·9	45·9	54·4	64·6	60·2	42·5	52·2	64·6	64·6	Grain to 100 straw.
5·6	59·6	62·6	55·6	57·3	60·5	62·5	57·4	58·7	62·1	62·1	57·5	58·6	62·1	62·6	56·9	58·6	62·1	62·5	Wt. per bushel of grain, lbs.

ain, per Acre, lbs.

5	1439	2587	1472	2001	1977	2979	1503	2102	2437	3533	1480	2036	2384	3453	1507	2195	2413	3527	Fresh produce.
4	1208	2194	1236	1674	1658	2524	1254	1747	2043	3012	1237	1716	1995	2904	1258	1844	2027	2982	Dry matter.
6·2	26·9	37·3	24·1	33·5	33·3	45·2	22·2	33·4	39·2	52·4	22·3	34·3	39·9	48·8	23·5	37·2	39·5	51·3	Nitrogen.

Grain, per Acre, lbs.

·14	0·14	0·21	0·24	0·40	0·32	0·25	0·20	0·37	0·44	0·25	0·19	0·40	0·33	0·29	0·23	0·39	0·30	0·23	Ferric oxide.
·84	0·93	1·32	0·92	1·23	1·20	1·69	0·77	0·98	1·19	1·77	0·74	0·92	1·16	1·40	0·80	0·92	1·11	1·56	Lime.
·67	2·41	3·83	3·19	3·53	3·13	4·66	3·12	3·65	4·00	5·54	3·10	3·47	3·99	5·41	3·15	3·82	4·13	5·78	Magnesia.
·44	7·68	11·78	6·58	9·17	10·34	14·18	6·97	9·98	13·21	17·84	6·95	9·68	13·05	17·52	7·00	10·18	13·00	17·30	Potash.
·09	0·09	0·19	0·13	0·11	0·16	0·24	0·14	0·10	0·15	0·23	0·15	0·10	0·06	0·17	0·19	0·11	0·23	0·31	Soda.
·69	10·69	15·76	12·88	17·02	15·42	21·65	12·96	17·86	19·59	25·85	12·78	17·11	19·57	25·24	12·97	18·41	20·18	25·64	Phosphoric anhydride.
·23	0·63	0·81	0·04	0·30	0·53	0·54	0·13	0·08	0·41	0·92	0·08	0·19	0·34	0·57	0·06	0·37	0·33	0·67	Sulphuric anhydride.
ne	0·13	0·07	trace	0·02	0·02	trace	trace	0·01	trace	0·10	trace	0·01	0·02	trace	trace	0·02	0·01	0·06	Chlorine.
·26	0·23	0·29	0·23	0·33	0·30	0·31	0·23	0·27	0·21	0·32	0·18	0·25	0·27	0·34	0·16	0·37	0·19	0·28	Silica.
·36	22·93	34·26	24·21	32·11	31·42	43·52	24·52	33·30	39·20	52·82	24·17	32·13	38·79	50·94	24·56	34·59	39·48	51·83	Total.
—	0·03	0·02	—	—	—	—	—	—	—	0·02	—	—	—	—	—	—	—	0·01	Deduct O = Cl.
·36	22·90	34·24	24·21	32·11	31·42	43·52	24·52	33·30	39·20	52·80	24·17	32·13	38·79	50·94	24·56	34·59	39·48	51·82	Total.

aw, per Acre, lbs.

	2130	3481	3081	3517	2797	4233	3257	3847	3663	5443	3222	3743	3693	5739	3547	4202	3737	5459	Fresh produce.
·7	1819	2930	2557	2951	2389	3538	2732	3206	3081	4534	2674	3129	3095	4746	2958	3516	3173	4537	Dry matter.
	11·5	10·3	11·8	12·7	12·4	15·6	12·8	10·6	12·3	16·8	13·1	9·1	12·4	11·9	16·3	12·7	13·0	12·2	Nitrogen.

Straw, per Acre, lbs.

·76	0·47	0·35	1·65	1·43	0·77	1·17	1·63	1·00	0·87	0·79	1·36	2·06	0·83	0·72	1·39	0·67	0·95	0·82	Ferric oxide.
·98	7·25	10·95	9·01	8·88	8·78	14·32	8·42	8·03	9·96	16·46	7·68	7·06	8·79	12·41	9·11	9·81	9·54	15·34	Lime.
·30	2·05	2·75	2·59	2·25	2·31	4·30	2·62	2·27	2·56	4·82	2·37	2·21	2·24	3·93	2·65	3·01	3·35	4·87	Magnesia.
·00	14·55	22·57	7·98	12·67	16·78	18·05	21·88	23·82	33·33	41·97	22·07	29·54	46·94	58·39	24·29	32·62	36·29	46·34	Potash.
·84	0·97	0·83	1·93	1·71	1·97	3·17	1·01	1·23	1·00	2·63	0·87	0·61	0·43	1·46	1·11	0·74	0·68	2·08	Soda.
·58	2·64	2·73	5·01	4·40	4·04	5·43	5·57	4·36	4·61	4·53	5·39	4·55	4·70	4·91	5·93	5·56	4·80	4·45	Phosphoric anhydride.
·28	6·55	6·13	2·53	4·16	6·56	7·13	3·82	4·65	8·08	7·99	3·57	4·87	8·83	7·48	4·38	5·28	8·43	7·92	Sulphuric anhydride.
·71	2·38	5·62	1·03	1·94	3·25	5·74	3·21	4·29	8·12	10·14	3·30	5·34	12·80	11·05	3·56	5·41	8·78	11·78	Chlo ine.
·39	47·60	107·67	124·50	103·07	83·46	135·82	118·08	96·43	93·85	154·83	109·94	105·87	91·91	151·88	119·61	98·31	98·99	152·20	Silica.
·84	84·46	159·60	156·23	140·51	127·92	195·13	166·24	146·08	162·38	244·16	156·55	162·11	177·47	255·23	172·03	161·41	171·81	245·80	Total.
·39	0·54	1·27	0·23	0·44	0·75	1·29	0·73	0·99	1·84	2·29	0·75	1·21	2·89	3·18	0·80	1·23	1·98	2·65	Deduct O = Cl.
·45	83·92	158·33	156·00	140·07	127·17	193·84	165·51	145·09	160·54	241·87	155·80	160·90	174·58	252·05	171·23	160·18	169·83	243·15	Total.

d Straw), per Acre, lbs.

	3569	6068	4553	5518	4774	7212	4760	5949	6100	8976	4702	5779	6077	9192	5054	6397	6150	8986	Fresh produce.
9	3027	5124	3793	4625	4047	6062	3986	4953	5124	7546	3911	4845	5090	7650	4216	5360	5200	7519	Dry matter.
	38·4	47·6	35·9	46·2	45·7	60·8	35·0	44·0	51·5	69·2	35·4	43·4	52·3	60·7	39·8	49·9	52·5	63·5	Nitrogen.

uce (Grain and Straw), per Acre, lbs.

90	0·61	0·56	1·89	1·83	1·09	1·42	1·88	1·37	1·31	1·04	1·55	2·46	1·16	1·01	1·62	1·06	1·25	1·05	Ferric oxide.
82	8·18	12·27	9·93	10·11	9·98	16·01	9·19	9·01	11·15	18·23	8·42	7·98	9·95	13·81	9·91	10·73	10·65	16·90	Lime.
97	4·46	6·58	5·78	5·78	5·44	8·96	5·74	5·92	6·56	10·37	5·47	5·68	6·23	9·34	5·80	6·83	7·48	10·65	Magnesia.
44	22·23	34·35	14·56	21·84	27·12	32·23	28·85	33·80	46·64	59·80	29·02	39·22	59·99	75·91	31·29	42·80	49·29	63·64	Potash.
93	1·06	1·02	2·06	1·82	2·13	3·41	1·15	1·33	1·15	2·86	1·02	0·71	0·49	1·63	1·30	0·85	0·91	2·39	Soda.
27	13·33	18·49	17·89	21·42	19·46	27·08	18·53	22·22	24·20	30·38	18·17	21·66	24·27	30·15	18·90	23·97	24·98	30·09	Phosphoric anhydride.
51	7·18	6·94	2·87	4·46	7·09	7·67	3·95	4·72	8·49	8·91	3·65	5·06	9·17	8·05	4·44	5·65	8·76	8·59	Sulphuric anhydride.
71	2·51	5·69	1·03	1·96	3·27	5·74	3·21	4·30	8·12	10·24	3·30	5·35	12·82	14·05	3·56	5·43	8·79	11·84	Chlorine.
65	47·83	107·96	124·73	103·40	83·76	136·13	118·31	96·70	94·06	155·15	110·12	106·12	92·18	152·22	119·77	98·68	92·18	152·48	Silica.
20	107·39	193·86	180·44	172·62	159·34	238·65	190·76	179·38	201·58	296·98	180·72	194·24	216·26	306·17	196·59	196·00	211·29	297·63	Total.
39	0·57	1·29	0·23	0·44	0·75	1·29	0·73	0·99	1·84	2·31	0·75	1·21	2·89	3·18	0·80	1·23	1·98	2·66	Deduct O = Cl.
81	106·82	192·57	180·21	172·18	158·59	237·36	190·03	178·39	199·74	294·67	179·97	193·03	213·37	302·99	195·79	194·77	209·31	294·97	Total.

Composition of the Ash of Wheat-Grain, and of Wheat-

Appendix-Table XIII.—General Characters of the Produce, and *Percentage* mixed Samples of the Grain, and proportionally mixed Samples of the differently manured Plots in each Case.

Plots and manures.	2. Farmyard manure.		3. Unmanured.		5b. Mixed min. man.		7b. Mixed min. and amm.		10a. Amm. salts alone.	
	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.
Grain to 100 straw...	56·5	62·7	56·8	71·0	59·2	67·9	52·7	59·9	52·4	66·3
Weight per bushel of grain, lbs.	58·8	61·3	55·8	54·9	57·2	60·5	57·8	60·7	55·1	59·1
Composition of the Grain, per cent.										
Dry matter	84·00	84·17	83·63	84·23	83·60	84·27	84·19	84·45	84·07	85·06
Nitrogen in dry matter	2·05	1·84	1·98	1·70	1·95	1·71	2·09	1·85	2·07	1·90
Ash (pure) in dry matter	2·06	1·92	2·08	2·00	2·10	2·03	1·99	1·89	1·88	1·72
Composition of the Grain-Ash (pure), per cent.										
Ferric oxide	0·53	0·45	0·72	0·57	0·63	0·52	0·71	0·56	0·73	0·61
Lime	2·49	2·59	3·13	3·22	2·66	2·82	2·79	2·94	3·90	4·35
Magnesia	10·93	10·97	10·44	10·52	10·54	10·65	10·62	10·71	10·42	10·89
Potash	31·69	32·20	33·52	33·17	32·34	32·76	32·87	33·42	34·01	34·12
Soda	0·22	0·16	0·23	0·13	0·26	0·10	0·20	0·12	0·18	0·22
Phosphoric anhydride.	52·81	52·16	49·83	50·30	51·74	50·85	50·95	50·14	46·29	45·79
Sulphuric anhydride.	0·55	0·89	1·40	1·44	0·82	1·69	1·16	1·46	2·84	3·03
Chlorine	0·01	0·02	0·03	0·07	0·01	0·02	0·01	0·01	0·59	0·42
Silica	0·77	0·56	0·71	0·60	1·00	0·59	0·69	0·64	1·17	0·66
Total	100·00	100·00	100·01	100·02	100·00	100·00	100·00	100·00	100·13	100·09
Deduct O = Cl	—	—	0·01	0·02	—	—	—	—	0·13	0·09
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Composition of the Straw, per cent.										
Dry matter	84·03	84·08	83·96	84·47	84·09	84·26	83·75	83·92	84·01	84·58
Nitrogen in dry matter	0·50	0·43	0·54	0·47	0·59	0·44	0·56	0·43	0·58	0·55
Ash (pure) in dry matter	6·44	6·55	6·08	6·68	6·45	6·91	5·43	5·11	5·27	5·46
Composition of the Straw-Ash (pure), per cent.										
Ferric oxide	0·45	0·29	0·73	0·65	0·74	0·66	0·56	0·34	0·64	0·42
Lime	3·96	4·25	5·03	5·12	4·00	4·20	5·15	6·00	5·93	7·41
Magnesia	1·27	1·45	1·49	1·56	1·26	1·44	1·46	1·83	1·63	2·02
Potash	19·87	19·60	15·88	14·83	18·76	17·86	23·65	24·64	18·15	14·23
Soda	0·11	0·15	0·32	0·21	0·14	0·21	0·23	0·16	0·85	0·84
Phosphoric anhydride.	3·34	3·43	3·09	3·11	3·93	4·12	2·90	2·98	3·05	2·79
Sulphuric anhydride.	3·40	2·93	4·11	3·57	4·32	4·70	4·48	4·28	5·05	4·86
Chlorine	3·30	3·46	2·01	2·25	2·43	2·46	4·56	5·64	2·87	2·49
Silica	65·05	65·22	67·80	69·21	64·97	64·90	58·04	55·40	62·48	65·50
Total	100·75	100·78	100·46	100·51	100·55	100·55	101·03	101·27	100·65	100·56
Deduct O = Cl	0·75	0·78	0·46	0·51	0·55	0·55	1·03	1·27	0·65	0·56
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

Straw, grown at Rothamsted, year after year on the same Land.

Composition of the Ash (excluding Sand and Charcoal), of proportionally Straw, of ten Years, 1852–1861, and of ten Years, 1862–1871, from ten

10b. Amm. salts alone.		11b. Amm. and superph.		12b. Amm., superph., and soda.		13b. Amm., superph., and pot.		14b. Amm., superph., and magn.		Plots and manures.
10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	
53·2	66·5	55·5	64·5	54·5	63·3	55·9	59·9	53·4	64·5	Grain to 100 straw.
56·3	59·6	55·9	58·9	58·0	60·4	58·3	61·2	58·0	60·6	Weight per bushel of grain, lbs.

Composition of the Grain, per cent.

83·97	85·11	83·96	85·00	83·86	85·07	84·10	84·88	83·93	84·91	Dry matter.
2·07	1·82	2·07	1·84	2·03	1·80	1·99	1·74	2·05	1·75	Nitrogen } in dry
1·88	1·75	1·96	1·79	1·97	1·84	1·95	1·86	1·97	1·87	Ash (pure) } matter.

Composition of the Grain-Ash (pure), per cent.

0·67	0·56	0·61	0·46	0·56	0·52	0·66	0·62	0·72	0·53	Ferric oxide.
3·41	4·17	3·87	4·31	2·97	3·57	2·88	2·96	2·87	3·41	Lime.
10·58	10·37	10·52	10·59	10·57	10·61	10·50	10·54	10·70	10·95	Magnesia.
33·92	34·12	31·73	32·10	32·77	33·33	32·93	33·52	32·57	33·06	Potash.
0·23	0·17	0·11	0·26	0·19	0·20	0·14	0·14	0·18	0·10	Soda.
48·59	47·04	50·76	49·67	50·96	50·01	51·46	50·18	51·55	50·30	Phosphoric anhydride.
1·69	2·26	1·56	1·91	1·37	1·18	0·71	1·43	0·73	1·00	Sulphuric anhydride.
0·16	0·27	0·01	0·18	0·01	0·01	0·01	0·01	0·01	0·01	Chlorine.
0·78	0·60	0·83	0·56	0·60	0·57	0·71	0·60	0·67	0·64	Silica.
100·03	100·06	100·00	100·04	100·00	100·00	100·00	100·00	100·00	100·00	Total.
0·03	0·06	—	0·04	—	—	—	—	—	—	Deduct O = Cl.
100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	Total.

Composition of the Straw, per cent.

83·82	84·53	84·03	83·88	83·61	84·27	83·37	84·12	83·97	84·03	Dry matter.
0·56	0·56	0·57	0·58	0·49	0·42	0·49	0·48	0·53	0·46	Nitrogen } in dry
5·11	5·08	5·41	5·24	5·25	5·32	5·35	5·32	5·31	5·15	Ash (pure) } matter.

Composition of the Straw-Ash (pure), per cent.

0·34	0·43	0·58	0·46	0·52	0·39	0·50	0·32	0·48	0·41	Ferric oxide.
5·92	8·02	5·94	8·56	5·29	7·27	5·22	5·91	5·27	6·90	Lime.
1·65	2·24	1·63	2·26	1·46	1·93	1·38	1·66	1·55	2·18	Magnesia.
19·39	14·81	14·77	14·08	20·05	17·20	24·10	25·00	21·95	18·54	Potash.
0·58	1·09	1·06	1·96	0·53	1·11	0·21	0·06	0·32	0·73	Soda.
2·97	2·55	3·39	3·63	3·24	3·14	2·98	2·97	2·85	3·24	Phosphoric anhydride.
4·58	4·40	4·35	4·63	4·46	4·07	4·55	3·89	4·60	4·16	Sulphuric anhydride.
3·18	3·30	2·45	3·75	3·58	3·73	4·75	5·69	4·29	4·05	Chlorine.
61·61	63·90	66·39	61·51	61·67	62·00	57·39	55·79	59·66	60·70	Silica.
100·72	100·74	100·56	100·84	100·80	100·84	101·08	101·29	100·97	100·91	Total.
0·72	0·74	0·56	0·84	0·80	0·84	1·08	1·29	0·97	0·91	Deduct O = Cl.
100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	Total.

Composition of the Ash of Wheat-Grain, and of Wheat-

Appendix-Table XIV.—General Characters of the Produce, and Amounts of 100° C.), of proportionally mixed Samples of the Grain, and proportionally 1862–1871; from ten differently manured Plots in each Case.

Plots and manures.	2. Farmyard manure.		3. Unmanured.		5b. Mixed min. man.		7b. Mixed min. and amm.		10a. Amm. salts alone.	
	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.
Gr. to 100 stw.	56·5	62·7	56·8	71·0	59·2	67·9	52·7	59·9	52·4	66·3
Wt. per bush. grain, lbs.	58·8	61·3	55·8	59·4	57·2	60·5	57·8	60·7	55·1	59·1

Per 1000 *Dry Matter of Grain.*

Fresh produce Nitrogen	1190 20·5	1188 18·4	1195 19·8	1187 17·0	1197 19·5	1186 17·1	1188 20·9	1184 18·5	1190 20·7	1176 19·0
Ferric oxide	0·11	0·09	0·15	0·11	0·13	0·11	0·14	0·11	0·14	0·11
Lime	0·51	0·50	0·65	0·65	0·56	0·57	0·55	0·56	0·73	0·75
Magnesia	2·25	2·10	2·17	2·11	2·21	2·16	2·11	2·03	1·96	1·88
Potash	6·52	6·18	6·98	6·65	6·79	6·66	6·53	6·33	6·39	5·87
Soda	0·05	0·03	0·05	0·03	0·06	0·02	0·04	0·02	0·03	0·04
Phosp. anhyd.	10·87	10·01	10·37	10·07	10·86	10·35	10·12	9·49	8·70	7·89
Sulph. anhyd.	0·11	0·17	0·29	0·29	0·17	0·35	0·23	0·28	0·53	0·52
Chlorine	trace	trace	trace	0·01	trace	0·01	trace	trace	0·11	0·07
Silica	0·16	0·11	0·15	0·12	0·21	0·12	0·14	0·12	0·22	0·11
Total	20·58	19·19	20·81	20·04	20·99	20·35	19·86	18·94	18·81	17·24
Deduct O=Cl	—	—	—	—	—	—	—	—	0·02	0·02
Total	20·58	19·19	20·81	20·04	20·99	20·35	19·86	18·94	18·79	17·22

Per 1000 *Dry Matter of Straw.*

Fresh produce Nitrogen	1190 5·0	1189 4·3	1191 5·4	1184 4·7	1189 5·9	1187 4·4	1194 5·6	1192 4·3	1190 5·8	1182 5·5
Ferric oxide	0·29	0·19	0·44	0·43	0·48	0·45	0·30	0·17	0·34	0·23
Lime	2·55	2·78	3·06	3·42	2·58	2·90	2·80	3·06	3·13	4·04
Magnesia	0·81	0·95	0·91	1·04	0·81	0·99	0·79	0·94	0·86	1·10
Potash	12·80	12·83	9·65	9·91	12·09	12·34	12·84	12·58	9·57	7·76
Soda	0·07	0·10	0·19	0·14	0·09	0·14	0·12	0·08	0·45	0·46
Phosp. anhyd.	2·15	2·25	1·88	2·08	2·53	2·84	1·57	1·52	1·61	1·52
Sulph. anhyd.	2·19	1·92	2·49	2·39	2·78	3·25	2·43	2·19	2·66	2·66
Chlorine	2·13	2·27	1·22	1·50	1·57	1·70	2·48	2·88	1·51	1·36
Silica	41·91	42·71	41·19	46·25	41·88	44·83	31·50	28·29	32·94	35·75
Total	64·90	66·00	61·03	67·16	64·81	69·44	54·83	51·71	53·07	54·88
Deduct O=Cl	0·48	0·51	0·28	0·34	0·36	0·38	0·56	0·65	0·34	0·30
Total	64·42	65·49	60·75	66·82	64·45	69·06	54·27	51·06	52·73	54·58

Per 1000 *Dry Matter of Total Produce* (*Grain and Straw*).

Fresh produce Nitrogen	1190 10·6	1189 9·7	1193 10·6	1185 9·8	1192 10·9	1187 9·5	1192 10·9	1183 9·6	1190 10·9	1180 10·9
Ferric oxide	0·22	0·15	0·34	0·30	0·35	0·31	0·25	0·15	0·27	0·18
Lime	1·82	1·90	2·19	2·27	1·83	1·96	2·02	2·12	2·30	2·73
Magnesia	1·33	1·40	1·37	1·48	1·33	1·47	1·25	1·35	1·24	1·41
Potash	10·54	10·27	8·68	8·55	10·12	10·04	10·65	10·23	8·48	7·01
Soda	0·06	0·07	0·14	0·09	0·07	0·09	0·09	0·06	0·31	0·29
Phosp. anhyd.	5·30	5·24	4·94	5·40	5·62	5·88	4·53	4·52	4·04	4·07
Sulph. anhyd.	1·44	1·25	1·70	1·52	1·82	2·07	1·67	1·47	1·93	1·80
Chlorine	1·36	1·39	0·78	0·88	0·99	1·01	1·62	1·80	1·03	0·84
Silica	26·82	26·28	26·35	27·13	26·44	26·74	20·64	17·69	21·69	21·49
Total	48·90	47·95	46·49	47·62	48·57	49·57	42·72	39·39	41·29	39·82
Deduct O=Cl	0·31	0·31	0·18	0·20	0·22	0·22	0·37	0·41	0·23	0·19
Total	48·59	47·64	46·31	47·42	48·35	49·35	42·35	38·98	41·06	39·63

Straw, grown at Rothamsted, year after year on the same Land.

Nitrogen, Ash-Constituents, and Total Ash (pure), *per* 1000 *Dry Matter* (at mixed Samples of the Straw, of ten Years, 1852–1861, and of ten Years

10b. Amm. salts alone.		11b. Amm. and superph.		12b. Amm., superph., and soda.		13b. Amm., superph., and pot.		14b. Amm., superph., and magn.		Plots and manures.
10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1852-'61.	10 years, 1862-'71.	10 years, 1862-'61.	10 years, 1862-'71.	
53·2	66·5	55·5	64·5	54·5	63·3	53·9	59·9	53·4	64·5	Gr. to 100 stw.
56·3	59·6	55·9	58·9	58·0	60·4	58·3	61·2	58·0	60·6	Wt. per bush. grain, lbs.

Per 1000 *Dry Matter of Grain.*

1192	1172	1191	1177	1192	1176	1189	1178	1192	1177	Fresh produce.
20·7	18·2	20·7	18·4	20·3	18·0	19·9	17·4	20·5	17·5	Nitrogen.
0·13	0·10	0·12	0·08	0·11	0·09	0·13	0·11	0·14	0·10	Ferric oxide.
0·64	0·73	0·76	0·77	0·58	0·66	0·56	0·55	0·56	0·64	Lime.
1·99	1·90	2·06	1·90	2·08	1·95	2·05	1·96	2·11	2·04	Magnesia.
6·39	5·98	6·22	5·76	6·46	6·14	6·43	6·22	6·41	6·16	Potash.
0·04	0·03	0·02	0·05	0·04	0·04	0·03	0·03	0·04	0·02	Soda.
9·16	8·24	9·95	8·92	10·05	9·21	10·05	9·31	10·15	9·38	Phosp. anhyd.
0·32	0·39	0·31	0·34	0·27	0·22	0·14	0·27	0·15	0·19	Sulph. anhyd.
0·03	0·05	trace	0·03	trace	trace	trace	trace	trace	trace	Chlorine.
0·15	0·11	0·16	0·10	0·12	0·10	0·14	0·11	0·13	0·12	Silica.
18·85	17·53	19·60	17·95	19·71	18·42	19·53	18·56	19·69	18·65	Total.
0·01	0·01	—	0·01	—	—	—	—	—	—	Deduct O=Cl.
18·84	17·52	19·60	17·94	19·71	18·42	19·53	18·56	19·69	18·65	Total.

Per 1000 *Dry Matter of Straw.*

1193	1183	1190	1192	1196	1187	1200	1189	1191	1190	Fresh produce.
5·6	5·6	5·7	5·8	4·9	4·2	4·9	4·8	5·3	4·6	Nitrogen.
0·43	0·22	0·31	0·24	0·27	0·21	0·26	0·17	0·26	0·21	Ferric oxide.
3·02	4·08	3·22	4·48	2·78	3·86	2·80	3·15	2·80	3·56	Lime.
0·84	1·14	0·88	1·18	0·77	1·03	0·74	0·88	0·82	1·13	Magnesia.
9·90	7·53	8·00	7·37	10·54	9·14	12·90	13·29	11·65	9·55	Potash.
0·30	0·56	0·57	1·03	0·28	0·59	0·11	0·03	0·17	0·37	Soda.
1·52	1·29	1·84	1·90	1·70	1·66	1·59	1·58	1·51	1·67	Phosp. anhyd.
2·34	2·23	2·35	2·42	2·34	2·17	2·43	2·06	2·45	2·14	Sulph. anhyd.
1·62	1·67	1·33	1·97	1·88	1·99	2·55	3·03	2·28	2·09	Chlorine.
31·47	32·47	35·94	32·20	32·39	32·96	30·70	29·66	31·69	31·28	Silica.
51·44	51·19	54·44	52·79	52·95	53·61	54·08	53·85	53·63	52·00	Total.
0·36	0·37	0·30	0·44	0·42	0·45	0·58	0·68	0·51	0·47	Deduct O=Cl.
51·08	50·82	54·14	52·35	52·53	53·16	53·50	53·17	53·12	51·53	Total.

Per 1000 *Dry Matter of Total Produce* (*Grain and Straw*).

1193	1179	1191	1186	1195	1183	1196	1185	1191	1185	Fresh produce.
10·8	10·7	11·1	10·8	10·3	9·6	10·2	9·5	10·6	9·7	Nitrogen.
0·32	0·17	0·25	0·18	0·22	0·16	0·22	0·15	0·22	0·17	Ferric oxide.
2·20	2·73	2·34	3·02	2·00	2·61	2·01	2·17	2·02	2·41	Lime.
1·24	1·45	1·30	1·47	1·23	1·39	1·20	1·29	1·27	1·49	Magnesia.
8·68	6·90	7·36	6·73	9·10	7·97	10·62	10·63	9·83	8·22	Potash.
0·21	0·35	0·38	0·64	0·19	0·37	0·08	0·03	0·12	0·23	Soda.
4·17	4·08	4·73	4·67	4·65	4·61	4·57	4·49	4·52	4·71	Phosp. anhyd.
1·64	1·50	1·62	1·60	1·61	1·41	1·62	1·38	1·65	1·37	Sulph. anhyd.
1·07	1·02	0·86	1·20	1·22	1·21	1·65	1·89	1·49	1·26	Chlorine.
20·59	19·47	23·17	19·51	20·99	20·15	19·94	18·53	20·71	18·98	Silica.
40·12	37·67	42·01	39·02	41·21	39·88	41·91	40·56	41·83	38·84	Total.
0·24	0·23	0·19	0·27	0·28	0·27	0·37	0·43	0·34	0·28	Deduct O=Cl.
39·88	37·44	41·82	38·75	40·93	39·61	41·54	40·13	41·49	38·56	Total.

Composition of the Ash of Wheat-Grain, and of Wheat-

Appendix-Table XV.—General Characters of the Produce, and Quantities of Fresh Produce, mixed Samples of the Grain, and proportionally mixed Samples of the Straw, of ten Years,

Plots and manures.	2. Farmyard manure.		3. Unmanured.		5b. Mixed min. man.		7b. Mixed min. and amm.		10a. Amm. salts alone.	
	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.
Gr. to 100 stw.	56·5	62·7	56·8	71·0	59·2	67·9	52·7	59·9	52·4	66·3
Wt. per bush. grain, lbs.	58·8	61·3	55·8	59·4	57·2	60·5	57·3	60·7	55·1	59·1

Produce of Grain, per Acre, lbs.

Fresh produce	2145	2385	944	881	1163	1007	2163	2309	1318	1553
Dry matter ...	1802	2008	790	742	972	849	1821	1950	1108	1321
Nitrogen	36·9	36·9	15·6	12·6	19·0	14·5	38·1	36·1	22·9	25·1
Ferric oxide ...	0·20	0·18	0·12	0·09	0·13	0·09	0·26	0·21	0·16	0·14
Lime	0·93	1·00	0·51	0·48	0·54	0·49	1·01	1·09	0·81	0·99
Magnesia	4·05	4·23	1·72	1·56	2·15	1·84	3·84	3·96	2·17	2·47
Potash	11·76	12·41	5·51	4·93	6·60	5·66	11·89	12·34	7·08	7·76
Soda	0·08	0·06	0·04	0·02	0·05	0·02	0·08	0·04	0·04	0·05
Phosp. anhyd.	19·59	20·10	8·19	7·47	10·55	8·78	18·42	18·52	9·64	10·42
Sulph. anhyd.	0·20	0·34	0·23	0·22	0·17	0·30	0·42	0·54	0·59	0·69
Chlorine.....	trace	0·01	trace	0·01	trace	trace	trace	trace	0·12	0·10
Silica	0·29	0·21	0·12	0·09	0·21	0·10	0·25	0·24	0·24	0·15
Total	37·10	38·54	16·44	14·87	20·40	17·28	36·17	36·94	20·85	22·77
Deduct O=Cl	—	—	—	—	—	—	—	—	0·03	0·02
Total	37·10	38·54	16·44	14·87	20·40	17·28	36·17	36·94	20·82	22·75

Produce of Straw, per Acre, lbs.

Fresh produce	3795	3803	1663	1241	1963	1483	4104	3857	2516	2341
Dry matter ...	3189	3198	1396	1048	1651	1249	3437	3237	2114	1980
Nitrogen	15·9	13·8	7·5	4·9	9·7	5·5	19·2	13·9	12·3	10·9
Ferric oxide ...	0·91	0·60	0·62	0·45	0·79	0·57	1·04	0·56	0·71	0·45
Lime	8·14	8·90	4·27	3·58	4·26	3·62	9·62	9·92	6·62	8·00
Magnesia	2·59	3·03	1·27	1·09	1·34	1·24	2·71	3·03	1·81	2·19
Potash	40·82	41·05	13·46	10·38	19·96	15·41	44·12	40·72	20·23	15·37
Soda	0·23	0·32	0·27	0·14	0·15	0·18	0·42	0·27	0·95	0·91
Phosp. anhyd.	6·86	7·19	2·62	2·19	4·19	3·55	5·41	4·91	3·39	3·01
Sulph. anhyd.	6·99	6·14	3·48	2·50	4·59	4·05	8·35	7·07	5·62	5·26
Chlorine	6·78	7·25	1·71	1·57	2·59	2·12	8·52	9·33	3·20	2·69
Silica	133·64	136·60	57·50	48·47	69·14	55·99	108·26	91·56	69·65	70·79
Total	206·96	211·08	85·20	70·37	107·01	86·73	188·45	167·37	112·18	108·67
Deduct O=Cl	1·53	1·63	0·39	0·35	0·59	0·48	1·92	2·09	0·72	0·61
Total	205·43	209·45	84·81	70·02	106·42	86·25	186·53	165·28	111·46	108·06

Total Produce (Grain and Straw), per Acre, lbs.

Fresh produce	5940	6188	2607	2122	3126	2490	6267	6166	3834	3894
Dry matter ...	4991	5206	2186	1790	2623	2098	5258	5187	3222	3301
Nitrogen	52·8	50·7	23·1	17·5	28·7	20·0	57·3	50·0	35·2	36·0
Ferric oxide ...	1·11	0·78	0·74	0·54	0·92	0·66	1·30	0·77	0·87	0·59
Lime	9·07	9·90	4·78	4·06	4·80	4·11	10·63	11·01	7·43	8·99
Magnesia	6·64	7·26	2·99	2·65	3·49	3·08	6·55	6·99	3·98	4·66
Potash	52·58	53·46	18·97	15·31	26·56	21·07	56·01	53·06	27·31	23·13
Soda	0·31	0·38	0·31	0·16	0·20	0·20	0·50	0·31	0·99	0·96
Phosp. anhyd.	26·45	27·29	10·81	9·66	14·74	12·33	23·83	23·43	13·03	13·43
Sulph. anhyd.	7·19	6·48	3·71	2·72	4·76	4·35	8·77	7·61	6·21	5·95
Chlorine.....	6·78	7·26	1·71	1·58	2·59	2·12	8·52	9·33	3·32	2·79
Silica	133·93	136·81	57·62	48·56	69·35	56·09	108·51	91·80	69·89	70·94
Total	244·06	249·62	101·64	85·24	127·41	104·01	224·62	204·31	133·03	131·44
Deduct O=Cl	1·53	1·63	0·39	0·35	0·59	0·48	1·92	2·09	0·75	0·63
Total	242·53	247·99	101·25	84·89	126·82	103·53	222·70	202·22	132·28	130·81

Straw, grown at Rothamsted, year after year on the same Land.

Dry Matter, Nitrogen, Ash-Constituents, and Total Ash (pure), *per Acre*, of proportionally 1852–1861, and ten Years, 1862–1871, from ten differently manured Plots in each Case.

10b. Amm. salts alone.		11b. Amm. and superph.		12b. Amm. superph. and soda.		13b. Amm. superph. and pot.		14b. Amm. superph. and magn.		Plots and manures.
10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	10 years, 1852–'61.	10 years, 1862–'71.	
53·2	66·5	55·5	64·5	54·5	63·3	53·9	59·9	53·4	64·5	Gr. to 100 stw.
56·3	59·6	55·9	58·9	58·0	60·4	58·3	61·2	58·0	60·6	Wt. per bush. grain, lbs.

Produce of Grain, per Acre, lbs.

1586	1707	1782	1799	2101	2173	2098	2305	2101	2210	Fresh produce.
1330	1456	1496	1529	1762	1848	1764	1956	1763	1877	Dry matter.
27·5	26·5	31·0	28·1	35·8	33·3	35·1	34·0	36·1	32·8	Nitrogen.
0·17	0·15	0·18	0·13	0·19	0·18	0·23	0·22	0·25	0·19	Ferric oxide.
0·85	1·06	1·13	1·18	1·03	1·22	0·99	1·07	1·00	1·20	Lime.
2·65	2·77	3·09	2·90	3·67	3·61	3·62	3·83	3·71	3·83	Magnesia.
8·50	8·70	9·30	8·80	11·39	11·34	11·34	12·17	11·30	11·57	Potash.
0·06	0·04	0·03	0·07	0·07	0·07	0·04	0·05	0·06	0·04	Soda.
12·18	12·00	14·88	13·63	17·70	17·02	17·73	18·21	17·89	17·61	Phosp. anhyd.
0·42	0·58	0·46	0·53	0·47	0·40	0·25	0·52	0·26	0·35	Sulph. anhyd.
0·04	0·07	trace	0·05	trace	trace	trace	trace	trace	trace	Chlorine.
0·20	0·16	0·25	0·16	0·21	0·19	0·24	0·22	0·23	0·22	Silica.
25·07	25·53	29·32	27·45	34·73	34·03	34·44	36·29	34·70	35·01	Total.
0·01	0·02	—	0·01	—	—	—	—	—	—	Deduct O=Cl.
25·06	25·51	29·32	27·44	34·73	34·03	34·44	36·29	34·70	35·01	Total.

Produce of Straw, per Acre, lbs.

2984	2565	3209	2790	3857	3431	3893	3848	3937	3425	Fresh produce.
2501	2168	2696	2340	3224	2891	3245	3237	3306	2878	Dry matter.
14·0	12·1	15·4	13·6	15·8	12·1	15·9	15·5	17·5	13·2	Nitrogen.
1·07	0·47	0·84	0·56	0·88	0·60	0·86	0·55	0·85	0·60	Ferric oxide.
7·56	8·84	8·68	10·49	8·95	11·17	9·07	10·18	9·25	10·24	Lime.
2·11	2·47	2·36	2·78	2·48	2·97	2·41	2·86	2·73	3·24	Magnesia.
24·76	16·32	21·57	17·24	33·99	26·43	41·84	43·04	38·53	27·50	Potash.
0·74	1·21	1·54	2·40	0·90	1·70	0·36	0·11	0·56	1·07	Soda.
3·80	2·80	4·96	4·44	5·48	4·81	5·15	5·10	5·00	4·80	Phosp. anhyd.
5·85	4·84	6·34	5·67	7·54	6·26	7·89	6·68	8·08	6·17	Sulph. anhyd.
4·06	3·63	3·59	4·60	6·05	5·74	8·27	9·81	7·54	6·00	Chlorine.
78·70	70·39	96·90	75·35	104·44	95·29	99·63	96·00	104·76	90·04	Silica.
128·65	110·97	146·78	123·53	170·71	154·97	175·48	174·33	177·30	149·62	Total.
0·91	0·81	0·81	1·03	1·35	1·29	1·87	2·21	1·70	1·35	Deduct O=Cl.
127·74	110·16	145·97	122·50	169·36	153·68	173·61	172·12	175·60	148·32	Total.

Total Produce (Grain and Straw), per Acre, lbs.

4570	4272	4991	4589	5958	5604	5991	6153	6038	5635	Fresh produce.
3831	3624	4192	3869	4986	4739	5009	5193	5069	4755	Dry matter.
41·5	38·6	46·4	41·7	51·6	45·4	51·0	49·5	53·6	46·0	Nitrogen.
1·24	0·62	1·02	0·69	1·07	0·78	1·09	0·77	1·10	0·79	Ferric oxide.
8·41	9·90	9·81	11·67	9·98	12·39	10·06	11·25	10·25	11·44	Lime.
4·76	5·24	5·45	5·68	6·15	6·58	6·03	6·69	6·44	7·07	Magnesia.
33·26	25·02	30·87	26·04	45·38	37·77	53·18	55·21	49·83	39·07	Potash.
0·80	1·25	1·57	2·47	0·97	1·77	0·40	0·16	0·62	1·11	Soda.
15·98	14·80	19·84	18·07	23·18	21·83	22·88	23·31	22·89	22·41	Phosp. anhyd.
6·27	5·42	6·80	6·20	8·01	6·66	8·14	7·20	8·34	6·52	Sulph. anhyd
4·10	3·70	3·59	4·65	6·05	5·74	8·27	9·81	7·54	6·00	Chlorine.
78·90	70·55	97·15	75·51	104·65	95·48	99·87	96·22	104·99	90·26	Silica.
153·72	136·50	176·10	150·98	205·44	189·00	209·92	210·62	212·00	184·67	Total.
0·92	0·83	0·81	1·04	1·35	1·29	1·87	2·21	1·70	1·35	Deduct O=Cl.
152·80	135·67	175·29	149·94	204·09	187·71	208·05	208·41	210·30	183·32	Total.

XLIV.—*Note on the General Law which governs the Expansibility of Liquids.*

By P. D. Hein.

In the April number of this Journal, Mendelejeff published a paper having for its object the determination of a general formula expressing the variations of volume which take place in liquids by increase in temperature.

The learned Russian physicist admits that if V indicates the volume of the liquid, t the temperature, and k a constant coefficient, then

$$\frac{dV}{dt} = kV^2.$$

or in integral—

$$V = (1 - kt)^{-1}.$$

It seemed to me that it would not be without interest to call attention to the fact that this is a particular case of the general formula to which I had been led before;* in admitting that the molecules attract one another in inverse proportion to a determined power of the distance. That formula has been written in the form—

$$V = \sqrt[1-m]{1 + (1 - m)at}.$$

Experiment alone can fix the value of m, but if we admit that $m = 2{\cdot}333$, numbers are obtained closely approximating to the observed values.

As Mendelejeff's formula corresponds with my general expression, where $m = 2$, it is unnecessary to observe that the only divergence which exists between our formulæ is in the determination of a coefficient; this may vary either in consequence of errors in observation, or on account of the difficulty of obtaining perfectly pure bodies; this comparatively slight divergence does not in any way affect the principle laid down.

Note.

As remarked by Mendelejeff, if it be admitted that $m = 2$, a close analogy exists between the formula which explains the variations of the volume of a gas and that which explains the variations of the volume of a liquid, the former having for expression $V = (1 + kt)^{+1}$, and the latter being of the form $V = (1 + kt)^{-1}$; I wish to show that

* *Bulletin of the Royal Academy of Sciences.* Brussels, 1882, p. 528.

this analogy follows naturally from my formula. In effect, if the molecules are separated the one from the other to such a distance that the influence of the distance might be considered as vanishing, or of little consideration, it becomes $m = 0$. On that hypothesis, my general formula is reduced to that which is admitted for a gas, and it becomes

$$V = 1 + at.$$

XLV.—*Melting Points of Certain Inorganic Substances.*

By Thos. Carnelley, D.Sc., University College, Dundee, and L. T. O'Shea, Firth College, Sheffield.

The following melting points have been determined by the method previously described by one of us (*Chem. Soc. J.*, **29**, 489; **33**, 273):—

	Melting point.	Mean.	Remarks.
Cuprous iodide, Cu_2I_2*	625 631	628	This compound decomposes in the air at a temperature near its m.p.; but if quickly heated its m.p. is reached before any perceptible decomposition has occurred.
Thallic oxide, Tl_2O_3	762 757 731	759	
Potassium bromate, $KBrO_3$ ..	436 431	434	Melts above 350°, *Watts's Dict.*, i, 672.
Sodium perchlorate, $NaClO_4$.	481 483	482	Prepared by saturating pure $HClO_4$ with the corresponding carbonates.
Silver perchlorate, $AgClO_4$ ..	485 486	486	
Thallium perchlorate, $TlClO_4$	500 502	501	
Barium perchlorate, $Ba(ClO_4)_2$	502 508	505	

Also the following alloys of the halogen compounds of silver, lead, and copper:—

* This compound and the alloys referred to below were prepared by Mr. G. F. Rodwell, *Phil. Trans.*, 1882, 1125.

	Melting point.	Mean.	Remarks.
(AgI,Ag_2Br_2,Ag_2Cl_2)	385 376 387	383	
$(AgI,AgBr,AgCl)$	329 335 330	331	
$(Ag_2I_2,AgBr,AgCl)$	328 323	326	
$(Ag_3I_3,AgBr,AgCl)$	355 354	354	
$(Ag_4I_4,AgBr,AgCl)$	382 378	380	
(AgI,PbI_2)	345	350	From bottom of cast rod.
	352		" "
	353		" "
	347		From top of ditto, after being once fused.
	352		Ditto, after frequent fusion.
(AgI,Cu_2I_2)	513 514 515	514	
$(2AgI,Cu_2I_2)$	491 501	496	
$(3AgI,Cu_2I_2)$	493 495	494	
$(4AgI,Cu_2I_2)$	479 492 505 496	493	Fused gradually.
$(12Ag,Cu_2I_2)$	514 514	514	

XLVI.—*On the Decomposition of Terpenes by Heat.*

By William A. Tilden, D.Sc. Lond., F.R.S., Professor of Chemistry in the Mason Science College, Birmingham.

So long ago as 1841, it was observed by Gay-Lussac and Larivière (*Compt. rend.*, **12**, 125) that when certain essential oils are subjected to heat, they yield a mixture of liquid products, some of which are as volatile as common ether. But beyond the very short preliminary notice, no further record of their experiments appears to have been published.

In 1868, Hlasiwetz* made the experiment of passing the vapour of turpentine oil through a red-hot iron tube filled with porcelain. From

* Obituary notice of Hlasiwetz, *Ber.*, **9**, 1991; also Hlasiwetz and Hinterberger, *Zeitschr. f. Chem.* [2], **4**, 380.

every 100 c.c. of turpentine oil he obtained on an average 60 c.c. of a liquid smelling like benzol, 16,800 c.c. of gas, and 2 grams of carbon deposited in the tube. The liquid submitted to fractional distillation gave between 60° and 70° a small quantity, the analysis of which led to the formula C_5H_8. This portion when redistilled began to boil about 30°, but soon a violent reaction set in, and without the further application of external heat, the temperature rose rapidly, and the contents of the flask ultimately exploded. Besides this peculiar and very volatile ingredient, fractions were obtained at intervals of 5°. More than one-third of the whole came over between 150° and 170°, that is, at about the boiling point of turpentine, and out of a litre of liquid submitted to distillation, only 40 c.c. remained when the temperature had been carried up to 200°.

Schultz (*Ber.*, **10**, 113) in 1877, by a perfectly similar process, using an iron tube heated to a dark red heat, obtained very different results. The most volatile substance he obtained was benzene, and accompanying this he identified toluene, metaxylene, naphthalene, phenanthrene, anthracene, and methyl-anthracene. It is probable, as I shall show later on, that the temperature of the tube in Schultz's experiments was much higher than in those of Hlasiwetz.

At temperatures considerably below redness, namely, from about 250° to 300°, it was shown by Berthelot (*Ann. Chim. Phys.* [3], **39**, 5) many years ago, that the terpenes undergo modification without altering in composition. They are gradually deprived of rotatory power, the boiling point is raised some 20°, and a large part is at the same time polymerised into products which boil at temperatures above 300°.

In view of the production from turpentine of a liquid apparently having the formula C_5H_8, and the transformation of isoprene, C_5H_8 (from india-rubber), into a terpene by heating it to 280°, having been accomplished by Bouchardat (*Compt. rend.*, **87** (1878), 654, and **89**, 361 and 1117), I was led to think further of the probable connection between the two series of hydrocarbons, and I commenced experiments in this direction more than two years ago.

I. *American Turpentine Oil.*

Commercial oil of turpentine was redistilled, and the portion passing over between 156° and 160° was reserved for the experiment. The turpentine to be operated upon was boiled in a copper flask provided with a proper safety tube to provide against accident in case obstruction should occur from deposition of carbon in the tube through which the vapour was passed. The vapour was delivered into an iron tube 1·2 metre long, heated for about three quarters of its length by

means of a combustion furnace to the lowest possible redness just visible in a darkened room. At the opposite end was attached (1) an empty bottle leading to (2) a second bottle surrounded by water (3), several feet of narrow tin pipe coiled into a spiral, which was surrounded by ice and salt (4), a flask surrounded by ice (5), a bottle containing ammoniacal cuprous chloride, and (6) a jet where the escaping gas was burnt, and the flame of which served to indicate the rate at which the vapour was coming through. In no case were more than a few grams of carbon deposited in the iron tube.

It was noticed that after some little liquid had collected in the two first bottles, practically nothing could be condensed by the freezing mixture, the heavier hydrocarbons apparently dissolving and retaining all but the permanently gaseous products.

A red precipitate was formed in the copper chloride, and the escaping gas burnt with a luminous and somewhat smoky flame.

Several distinct experiments were made in this manner upon quantities of turpentine varying from 1 litre to 4 litres.

Details of one operation will suffice. Four litres were used. The vapour of the whole having been passed through the iron tube once,* the total liquid product was collected and submitted to distillation. All that passed over below 140° was collected, whilst unaltered turpentine and less volatile hydrocarbons remained in the residue. The distillate (labelled A) measured 600 c.c.

In order to ascertain whether fresh turpentine or that which had already been once heated gave the larger yield of light hydrocarbons, the residue was returned to the copper boiler, and the vapour passed through the tube again, the product distilled as before, and the residue again subjected to heat. This process was repeated several times so long as any appreciable amount of distillate below 140° could be obtained from the liquid product. The lighter portions boiling up to 140° obtained from these successive operations were mixed together. The whole (labelled B) measured 675 c.c. Of the rest the total amount distilling between 140° and 200° was 850 c.c. It was slightly yellow, and optically inactive. It therefore contained no unchanged turpentine. The residue not distilling at 200° was of the consistence and appearance of treacle, and measured 650 c.c.

Of the 4000 c.c. of turpentine oil taken, the balance of 1225 c.c. not recovered is accounted for in the gas produced, and in slight loss by evaporation. A few grams of sooty carbon were found in the tube.

A. The 600 c.c. were distilled again in a flask provided with a very long bulb fractionater, the condenser being supplied with ice. 240 c.c. were obtained below 80°.

* It was estimated that 215 to 220 litres of gas were produced. It consists chiefly of hydrogen, but the vapours accompanying it deserve further investigation.

B. The 675 c.c. treated in the same way gave only 200 c.c. below 80°.

It will be shown presently that the chief volatile ingredient here is a pentine, C_5H_8, and it would seem, therefore, that the original terpene is more readily depolymerised than is the optically inactive isomeride (terpilene), which also results from the action of heat upon it. This will be again referred to.

The whole of the liquids were now submitted to a systematic fractional distillation.

1. *Fractions up to* 30°.—The lightest portions begin to boil somewhat below 20°, but the thermometer quickly runs up to 30°. Nothing definite has been isolated below this temperature, but from the production of a small quantity of a greenish-yellow precipitate when the liquid is shaken up with ammoniacal cuprous chloride, the presence of some acetylenic hydrocarbon may be inferred. The greater part consists of the pentine referred to in the next paragraph, holding in solution hydrocarbons which are gaseous at the temperature of the air.

2. *Fractions* 30° *to* 40°.—Some 250 c.c. were obtained which were resolved into a principal portion boiling between 33° and 37°, and smaller quantities of higher and lower fractions. This liquid smells like isoprene, the pentine from india-rubber (C. Greville Williams, *Phil. Trans.*, 1860, 241).

It gives no copper or silver compounds, and oxidises rapidly on exposure to the air. The result of this oxidation is a syrupy liquid, which often exhibits the peculiar spontaneous rise of temperature and explosive decomposition described by Hlasiwetz and by Greville Williams. I have had one explosion of this kind when redistilling some isoprene which had been kept some time.

It is very difficult to determine with certainty the boiling point of this hydrocarbon. After repeatedly fractionating the total quantity in my possession, the largest distillate was obtained near to 37°.

Analysis of Fraction 33—35°.

I. 0·1634 gram gave 0·1822 H_2O and 0·5217 CO_2.
II. 0·1010 „ „ 0·1147 „ „ 0·3242 „

	I.	II.	Mean.	C_5H_8.
Carbon	87·08	87·52	87·30	88·2
Hydrogen	12·36	12·57	12·46	11·8

The formula, C_5H_8, is adopted for reasons given hereafter, notwithstanding that the analytical numbers agree with the calculated percentages less closely than could be desired. With the greatest precautions for its protection, the hydrocarbon always leaves in the bulb

an oily film, which on heating swells up suddenly and leaves a black stain behind. Moreover, it is quite possible that notwithstanding repeated fractionation, the liquid analysed may have been contaminated with small quantities of a homologue or some other hydrocarbon. It was not thought worth while to make repeated combustions, as the identification of the hydrocarbon is more certainly accomplished in other ways.

The vapour-density was taken several times in steam by Hofmann's method.

	I.	II.	III.	IV.	V.
Boiling point.....	37—40°	33—35°	33—35°	37—38°	37—38°
Weight of liquid	0·0889	0·0997	0·1006	0·1038	0·1038
Obs. vol. of vapour, c.c.	64·8	64·0	72·6	68·5	69·0
Barometer, mm.	752	742	739·4	754·2	754·6
H (at 100°), mm.	310	235	287	256	258·5
Vapour-density.....	35·6	35·3	35·1	34·9	34·8

Vapour-density calculated from—

C_4H_6.	C_5H_8.	C_6H_{10}.
27	34	41

Conclusive proof of its composition was obtained by an examination of the polymerisation of this hydrocarbon by heat. A quantity of the fraction 33—35° was sealed up in tubes and heated at 250—280° for about twelve hours. No gas was evolved, but the liquid acquired a slight fluorescence. When submitted to distillation, a quantity of hydrocarbon apparently unaltered was recovered, but about half the volume distilled between 170° and 180°, whilst a small quantity of pale viscid colophene remained behind. The liquid (170—180°) was shaken up with saturated aqueous hydrochloric acid. After several days, a drop of the liquid gave very plainly Riban's reaction for terpene dihydrochloride with ferric chloride. It was therefore submitted to partial distillation in hydrochloric acid. The liquid remaining behind was then placed in a freezing mixture, and at a few degrees below zero it set into a crystalline mass. The distillate did not crystallise even at — 20° until a minute particle of terpilene dihydrochloride (made from turpentine) was introduced. Subsequently some of the crystals were separated and found to possess the same odour and melting point, 49°, as the dihydrochloride, $C_{10}H_{16}$,2HCl, prepared from turpentine.

There is now no doubt that the di-isoprene of Bouchardat (*loc. cit.*) and the dipentine I have just described, are identical with terpilene,

the optically inactive hydrocarbon into which the terpenes and citrenes are convertible (Tilden, *Ber.*, **12**, 1131).

In all probability also, the pentine from turpentine is identical with isoprene. I have carefully compared them together, and cannot observe any essential difference between them.

Both hydrocarbons combine violently with bromine forming a liquid *tetra*bromide in the form of a yellowish pungent oil, which does not solidify at − 20°. It is decomposed by distillation, and in contact with excess of bromine evolves hydrobromic acid.

Both hydrocarbons absorb hydrochloric acid gas eagerly, giving a mixture of monochloride and dichloride. The compounds prepared from isoprene have been described by Bouchardat (*loc. cit.*). Those prepared from the turpentine hydrocarbon resemble the isoprene chlorides. Both are slightly decomposed on distillation, with liberation of hydrochloric acid. A specimen of the dihydrochloride from the turpentine hydrocarbon distilled between 145° and 150°, and gave 48·0 per cent. of chlorine. The formula $C_5H_8,2HCl$ requires 50·3 per cent. Cl. This liquid when heated with water and oxide of lead to about 130°, is slowly decomposed, but the chief product is regenerated hydrocarbon, and no appreciable quantity of any alcoholic compound could be obtained.

Bouchardat mentions that the action of concentrated hydrochloric acid upon isoprene converts a portion of the hydrocarbon into caoutchouc. This substance is also formed from the turpentine hydrocarbon. It appears to be produced most readily from the oily polymeride, resulting from the action of heat. Contact with strong acids in the cold effects the change.

Both hydrocarbons are slowly acted upon by diluted sulphuric acid (1 vol. acid, 2 vols. water), but in contact with stronger acid (2 vols. to 1 vol. water), they evolve heat and are rapidly polymerised into terpilene mixed with colophene.

Chromic acid oxidises these hydrocarbons into carbonic, formic, and acetic acids. Nitric acid produces a large quantity of oxalic acid, together with a syrupy acid which has not been further examined for want of material.

3. *Fractions* 40—100°.—Very little was obtained below 70°, and this consisted partly of pentine. The portions boiling between 70° and 95° were shaken up with successive small quantities of strong sulphuric acid, and then washed and distilled. A very small quantity, 10—15 c.c., of benzene was isolated. Contact with the acid caused the production of a deep bluish-green colour similar to that which is given by the heptine, C_7H_{12}, from "spirit of resin" (Renard, *Compt. rend.*, **91**, 419; Morris, *Chem. Soc. J.*, **41**, 167).

A similar green and blue colour resulted from the action of strong

aqueous hydrochloric acid, not only upon this portion, but upon the partly purified fractions obtained at higher temperatures up to about 160°. The reaction is so marked, that there can be little doubt that this hydrocarbon is present. I have, however, been unsuccessful in attempts to isolate it by fractionation.

4. *Fractions* 100—130°.—From this portion some 70 c.c. of toluene were obtained and identified by conversion into dinitrotoluene melting at 70°.

5. *Fractions* 130—150°.—Fully three-fourths of the distillate obtained within these limits consisted of xylene. After treatment with sulphuric acid and washing, about 125 c.c. distilled between 135° and 140°. This hydrocarbon proved to consist wholly of metaxylene. When oxidised by a 5 per cent. chromic acid solution, it gave pure metatoluic acid melting at 109°, and subsequently isophthalic acid melting at 310—315°. It was also converted by a mixture of sulphuric and nitric acids into a trinitro-compound, which was sparingly soluble in spirit of wine, and the melting point of which was 182°.*

The various fractions boiling between 70° and 150° consist therefore of benzene, toluene, and a considerable quantity of metaxylene, these three constituting rather less than half of the entire volume; whilst the remainder consists partly of a hydrocarbon which is probably identical with the heptine of rosin spirit.

Small quantities of other hydrocarbons are present, but I have not succeeded in identifying them. It is highly probable, however, that they include a hexine, C_6H_{10}, homologous with and intermediate between the pentine and heptine referred to.

6. *Fractions* 150—180°.—Terpilene is present, as shown by the action of sulphuric or of hydrochloric acid, but on treating the portion which came over between 170° and 180° with small quantities of sulphuric acid, and then steam distilling, it yielded more than half its volume of cymene, the presence of which effectually prevented the isolation of the dihydrochloride of terpilene in a crystalline state. The cymene was soluble with very little blackening in ordinary sulphuric acid. The air-dried barium salt gave the following results on analysis:—

	I.	II.	III.	$(C_{10}H_{13}SO_3)_2Ba3H_2O$.
Water (at 135°).	7·97	7·92	—	8·75
Ba	—	23·30	23·18	22·20

The salt dried at 135° gave—

		Theory for $(C_{10}H_{13}SO_3)_2Ba$.
Ba	25·30	24·33

* The melting point of the trinitro-compound from metaxylene is given in the books as 176°, but as it was doubtless made from coal-tar xylene it was probably contaminated with other nitro-compounds.

Hence the sulphonate was apparently contaminated with a small quantity of some other salt containing less water and more barium. But that the hydrocarbon from which it was prepared is ordinary cymene there can be no doubt, as it yields abundance of paratoluic acid by oxidation with nitric acid.

The following is a summary of the results of the examination of the products of the action of heat upon ordinary turpentine oil.

4000 c.c. turpentine oil gave—

- 2125 c.c.
  - (Up to 140°) 1275 c.c.
    - (20—70°) 380 c.c. Yielded about 200 c.c. nearly pure pentine.
    - (70—100°) 160 c.c. 15 c.c. benzene with heptine, C_7H_{12}.
    - (100—120°) 170 c.c. 70 c.c. toluene, with heptine, C_7H_{12}.
    - (120—145°) 200 c.c. 150 c.c. metaxylene, with C_7H_{12}.
    - (145—170°) 845 c.c. Composed chiefly of cymene and terpilene, about equal volumes, with a little polyterpene.
  - (140—200°) 850 c.c.
    - (145—170°) 845 c.c. Composed chiefly of cymene and terpilene, about equal volumes, with a little polyterpene.
    - (170—190°) 290 c.c. Composed chiefly of cymene and terpilene, about equal volumes, with a little polyterpene.
    - Residue not distilled.
- 1875 c.c.
  - (Residue above 200°) ..... 650 c.c.
  - (Loss chiefly in form of gas) 1225 c.c.

Action of Higher Temperatures on Turpentine Oil.

When the vapour of turpentine oil is transmitted through the iron tube heated to redness visible in daylight, and to higher temperatures, the pentine is no longer found in the product. In that case, a large quantity of gas is evolved, and the most volatile constituent of the liquid product is benzene. I have not examined the less volatile hydrocarbons simultaneously produced, but I have no doubt the account given of them by Schultz (*loc. cit.*) is correct. They possess, however, very little interest in connection with the present inquiry, inasmuch as they evidently result from secondary reactions, and they consequently occur commonly among the products of the action of heat on many hydrocarbons.

Action of Heat on Citrenes, Terpilene, Colophene, and Camphene.

Oil of limes was employed as the source of a hydrocarbon to represent the *citrenes*. The portion boiling below 177° was taken, and the vapour of 340 c.c. passed through the iron tube exactly as in dealing with turpentine, keeping the temperature as low as possible. On

distilling the liquid an appreciable quantity of pentine was obtained agreeing in general properties with the product from turpentine.

About half a litre of *terpilene* was prepared by the action of diluted sulphuric acid on crystallised terpin. Treated in the same way as turpentine it appeared to undergo little change, and it was only when again passed through the tube, heated somewhat more strongly, that an appreciable quantity of volatile products were obtained. A portion of the pentine separated by fractionation had the characteristic smell, and a vapour-density determination proved its composition—

Weight of liquid	0·0909	
Observed vol. of vapour	71·30	c.c.
Barometer	746·00	mm.
H at 99°	319·00	mm.
Vapour-density	34·05	
Theory for C_5H_8	34·00	

Colophene (Armstrong and Tilden, *Chem. Soc. J.*, **35**, 748—749), prepared from turpentine by the action of strong sulphuric acid was next tried. It was freed from volatile camphenes, &c., by distillation first alone and then in steam. On account of its high boiling point, the vapour could not be generated in a separate boiler, and it was found more convenient to allow the liquid to drop slowly into the iron tube, heated as usual. 600 c.c. weighing 548 grams were taken. Some gas was given off, and 542 c.c. of liquid were recovered. But this gave very little of any product boiling below 180°. Transmitted again through the tube, heated to a somewhat higher temperature, decomposition took place, but the chief volatile products were benzene and its homologues.

Camphene, prepared from the monohydrochloride of turpentine oil, when heated strongly in sealed glass tubes is resolved into permanently liquid hydrocarbons. At higher temperatures some viscid colophene is produced at the same time. No pentine was obtained. This hydrocarbon deserves a further examination.

General Conclusions.

From the results described in this paper, the following general conclusions may be drawn:—

1. When ordinary turpentine oil is exposed to a temperature just short of redness, the greater part of it is transformed in four different ways.

a. By conversion into an optically inactive terpene.

b. By polymerisation into a "colophene."

c. By resolution into cymene and hydrogen, $C_{10}H_{16} = C_{10}H_{14} + H_2$.
d. By splitting up into 2 mols. of a pentine,* $C_{10}H_{16} = 2C_5H_8$.

These are probably the immediate changes which it undergoes, the small quantities of other hydrocarbons which are simultaneously produced being the result of secondary reactions arising from the further action of heat upon some of these.

2. The citrenes yield the same pentine, as also does terpilene, though less readily.

3. The pentine obtained from the terpenes is identical with isoprene.

4. This pentine is readily polymerised by heat into terpilene, $2C_5H_8 = C_{10}H_{16}$.

5. From the easy transformation of $2C_5H_8$ into $C_{10}H_{16}$, and *vice versâ*, it appears probable that the molecule of terpilene is composed symmetrically of two halves, $(C_5H_8) = (C_5H_8)$.†

6. The pentine from turpentine, or isoprene, as it may now be called, is a lower homologue, or isomeric with a lower homologue of heptine, from rosin spirit, which has been shown by Morris (*loc. cit.*) to be pretty certainly methyl-propyl-allene, $CH_3.CH:C:CH.C_3H_7$.

7. Just as the pentine is polymerisable by heat or by the action of sulphuric acid into a dipentine, so the heptine may be converted into a diheptine (Rénard, Tilden, and Morris). $C_{14}H_{24}$ is a liqnid boiling at 235° to 240°, and appears to have many of the properties of the terpenes. I intend at once to examine this compound further with the view of ascertaining whether it is entitled to rank as a true homologue of turpentine. We should then have two parallel series, the respective terms running as follows:—

C_nH_{2n-2}	C_nH_{2n-4}
C_3H_4	C_6H
C_4H_6	C_8H_{12}
C_5H_8	$C_{10}H_{16}$
C_6H_{10}	$C_{12}H_{20}$
C_7H_{12} &c.	$C_{14}H_{24}$ &c.

The alternate terms of the series of terpenes containing an uneven number of carbon-atoms might conceivably be produced by the union of an even with an odd term of the C_nH_{2n-2} series. Thus $C_5H_8 + C_6H_{10} = C_{11}H_{18}$.

* It may be noted here that Berthelot found pentane, C_5H_{12}, among the products of the action of hydriodic acid upon turpentine oil. (*Compt. rend.*, **67**, 327.)

† Much after the fashion of one of the diamylenes, which has been represented on less satisfactory evidence, by a symmetrical formula, such as $\begin{matrix}CH.CH_2(C_3H_7)\beta \\ \| \\ CH.CH_2(C_3H_7)\beta\end{matrix}$ (Schneider, *Annalen*, **157**, 185—226.)

8. Of the eight possible formulæ for pentines, three, namely the substituted acetylenes, are excluded from consideration, inasmuch as the particular compound here referred to gives no metallic derivatives. The formula for isoprene must be selected from the five following:—

Ethyl allene.....	$CH_3CH_2.CH:C:CH_2$
α-Dimethyl allene	$CH_3.CH:C:CH.CH_3$
β-Dimethyl allene.....	$(CH_3)_2C:C:CH_2$.
α-Methyl crotonylene ..	$CH_3.CH:CH.CH:CH_2$
β-Methyl crotonylene ..	$CH_2:C(CH_3).CH:CH_2$.

I have already pointed out in another journal (*Chem. News*, **46**, 1882, 121) the relation of some of these formulæ to the formulæ I proposed (*Chem. Soc. J.*, **33**, 80) some years ago for the natural terpenes, but beyond reaffirming my conclusion that the terpenes are in no sense aromatic compounds or constituted on the type of benzene, I prefer to refrain for the present from further speculation as to their probable constitution.

XLVII.—*On the Magnetic Rotary Polarisation of Compounds in Relation to their Chemical Constitution; with Observations on the Preparation and Relative Densities of the Bodies Examined.*

By W. H. Perkin, Ph.D., F.R.S.

About two years since I had the honour of bringing before this Society an account of a few experiments and observations I had made on the magnetic rotary polarisation of bodies, and referred to some of the work which had been done on this subject by other workers, especially by De la Rive and Becquerel. Attention was then drawn to the fact that no definite relationship had been discovered between the chemical constitution of substances and their power of rotating the plane of polarisation when under magnetic influence. I endeavoured also to show that no relationship of this kind was likely to be found by the usual method of calculating the results of the observations—which consists in comparing the magnetic rotary effect of unit-lengths of the fluid bodies—but that if unit-lengths of vapour could be examined some useful information might be obtained, because these lengths would be occupied by equal numbers of molecules. But as an examination of this kind would present very serious difficulties, it was shown how the same end might be attained by referring the results of the observations obtained by the examination of unit-lengths of fluids to the lengths of columns of liquid which would be formed by the condensation of unit-lengths of their vapours; in other words, to lengths related to each other in proportion to their molecular weight, making the necessary correction for difference of densities. This can be effected by the simple formula—

$$\frac{r \times Mw}{d},$$

r being the rotation observed, Mw the molecular weight, and d the relative density. This calculation having been made, both for the substance under examination, and also for the standard with which it is compared, it is only necessary to divide the result obtained from the former by that of the latter, and the product will be the "molecular coefficient of magnetic rotation," or, more briefly, the "molecular rotary power."

From the calculation in this way of the results which had been obtained by myself and others, it seemed that a definite relationship did exist between the magnetic rotary power and the chemical con-

stitution of bodies. As it appeared that results of this kind, likely to be of practical value to chemists, might be obtained by a more thorough investigation of this subject, I continued experimenting in this direction, and now give an account of the examination of about 140 different substances of the fatty series. It was my intention to include in this paper bodies of the aromatic as well as of the fatty series, but although I have examined many of them I found that it was necessary to postpone this part of the subject for the present. I hope, however, to take it up shortly.

Before speaking of the measurements which have been made, it will be necessary to describe the apparatus and the methods used in making them.

Two arrangements may be employed for submitting the products to be examined to magnetic influence. The first consists in placing the body between the pole pieces of an electromagnet. The second in placing it in the interior of a helix traversed by an electric current. All the observations described in this paper were made with an arrangement of the former kind. Experiments were made with a helix, but it was thought to possess several disadvantages: in the first place the rapid change of temperature, due to the heating of the wire, is a drawback, as it not only quickly changes the temperature of the substance under examination, but also causes the formation of convection currents, and thus makes the readings with the polariscope difficult and inaccurate; moreover, the amount of product required for examination is much larger,—an important consideration when rare bodies have to be examined.

The following is a description of the principal parts of the apparatus; the way in which they were arranged will be described afterwards.

The electromagnet employed was made by Ladd. It consists of two cylinders of soft iron 7·5 cm. in diameter and 38 cm. in length; these are fastened to a bed plate by strong bolts 2 cm. in diameter. The bed plate is 43 cm. long by 13 cm. wide and 1·5 cm. thick, this has a 2 cm. slot running along its centre through which the bolts of the cylinders pass, and by this arrangement their distance from each other can be varied at pleasure; each side of the bed plate is thickened by an iron bar fixed to it, 2·5 cm. thick and 4 cm. wide, so that practically it may be said that the bed plate consists of a plate 4 cm. thick with a groove 2·5 deep and 5 cm. wide, running along it lengthwise.

The wire used is 4 mm. in diameter (No. 10 B.W.G.), double covered; this is wound on thin brass bobbins fitting the cylinders. There are about 170 metres on each, or altogther 340 metres.

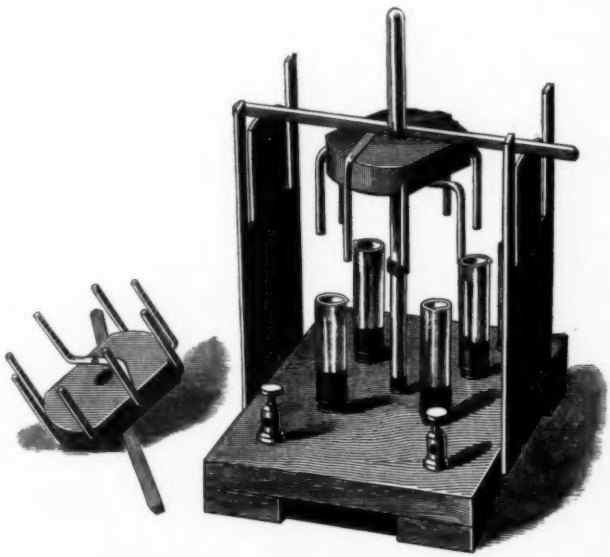
The two pole pieces are made of soft iron 7·5 cm. square and 11 cm.

long, one end being square and the other conical; they are pierced through the centre with a hole 2 cm. in diameter, which is contracted at one end by the introduction of a plug of soft iron 2·5 cm. long, perforated with a hole 6 mm. in diameter.

The battery power used with this electromagnet consists of twenty Groves' cells with platinums 10 × 20 cm.; these are arranged in two series of ten and coupled together. Worked in this way, they are more constant than when in single series, and keep cooler. When in use, they are immersed in a trough of cold water, and are charged with nitric acid, 1·42 sp. gr., and dilute sulphuric acid, 1 vol. acid to 6 vols. of water.

The commutator used at first had platinum contacts, but owing to their roughening by sparking, they were considered unsatisfactory. One was therefore made with mercury contacts, and as it has proved very serviceable for this kind of work, the following sketch of it is given (Fig. 1). From this it will be seen to consist of a wooden stand carrying four glass tubes, holding mercury, thick copper wires in connection with binding screws passing up into them. The arrangement for completing the circuit consists of a disk of boxwood

FIG. 1.



revolving on a central rod, and carrying two pairs of wires arranged so as to give a direct or reversed current. The ends of each pair can be dropped into the mercury tubes alternately by letting the cross bar

on the disk slide down the slits in the guides placed at the sides of the stand.

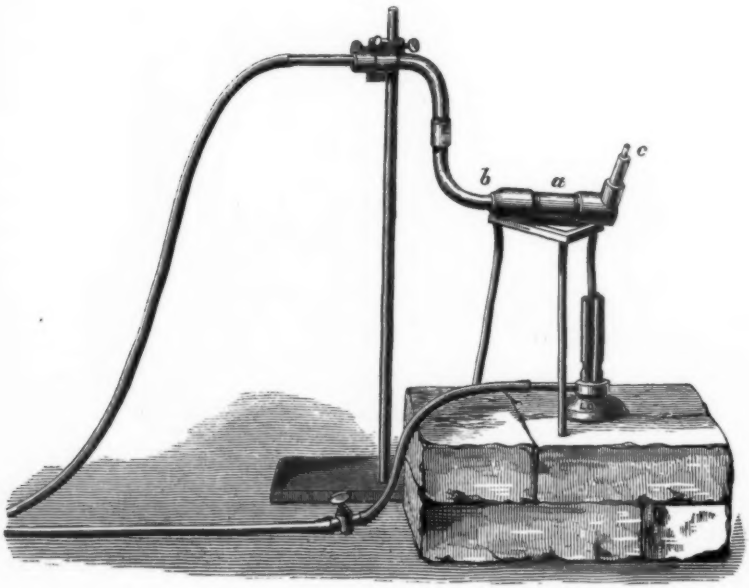
The Monochromatic Light employed.

All the measurements recorded in this paper were made for the D line, that is to say, by a flame illuminated by sodium. Experiments were also made with thallium and lithium, but as the amount of work to be done was so large, it was thought best to confine the attention, at first, to measurements by one light only. In the preliminary part of this investigation, the lamp generally supplied with saccharimeters was used, consisting of a powerful Bunsen burner having a long platinum spoon fitted to it, which can be filled with chloride of sodium and placed in the flame. This was found to be a very inconvenient arrangement for protracted work, not giving a sufficiently constant light, requiring frequent attention, and not always being sufficiently brilliant. A considerable number of experiments were made to overcome these difficulties, and eventually the following arrangement was devised, and has been found to work admirably. Its principle consists in burning a mixture of hydrogen and sodium vapour.

The apparatus is very simple, and is made out of ordinary wrought-iron gas tube. It will best be understood by the accompanying sketch, Fig. 2.

The centre part of the apparatus *a* consists of a short piece of iron

FIG. 2.



gas tubing 2 cm. internal diameter, provided with a thread on each end. On to one of these, a reducing socket is screwed, and to this two iron bends are attached; on to the other end, a reducing elbow is screwed, and into this a short piece of tubing furnished with a cast-iron fishtail burner *c*. The joints of this apparatus are made air-tight by means of the ordinary mixture of red and white lead used by engineers.

To charge this with sodium the bends are disconnected at *b*, and sodium inserted either in pieces or, preferably, as a rod hammered to the required thickness, and nearly as long as the tube will take. The bends are then replaced, red and white lead being used to make the joint tight.

When using the apparatus, it is usually supported by a tripod, and kept in its place with a clamp, as shown in the woodcut; the bend is connected to a bottle of compressed hydrogen by means of vulcanised tubing, the gas being passed slowly through the apparatus, which is heated with a triple Bunsen's burner. This should be kept under the elbow, and so as to heat the burner also, otherwise sodium will distil forward and be projected by the pressure of the hydrogen behind it. When the sodium becomes sufficiently heated, the hydrogen flame will become of an intense and brilliant yellow from the combustion of the sodium vapour it contains. This flame is quite under control, and can be made small or large by regulating the supply of hydrogen. To protect it from draughts, a small sheet-iron chimney with an aperture in the front is fitted to it. When once started, this apparatus will keep burning steadily for ten or twelve hours without any further attention, except to detach any sodium carbonate which may collect on the burner. A bottle containing about a cubic metre of hydrogen is generally enough for four or five days' work.

Thallium and indium give good monochromatic lights when volatilised with hydrogen and burnt.

A small Wurtz flask, filled with a solution of potassium dichromate to purify the light, has been found to act as a convenient condenser between the sodium light and polariser, as it can be easily held in a clamp by its delivery tube. A 4 per cent. solution of potassium dichromate has been found a suitable strength to use.

The tube holding the sodium requires at times to be cleaned out, as it gets clogged with oxide or hydrate of sodium, probably from moisture in the hydrogen. This operation requires great care, as the addition of water produces dangerous explosions. It is best, after removing the bends, to heat it sufficiently to melt any sodium it may contain, and to shake this out into petroleum; the tube should be then placed in an open space, and water projected into it from a distance, and fresh water added until all action is over.

General Arrangement of the Apparatus.

This is shown in Fig. 3. A is a strong stand, about 1·14 metres high, supporting the electromagnet B, which is laid on its side. This position is preferred to the upright one, because any currents of warm air arising from increase of temperature of the coils cannot then come in contact with the substances under examination. Two somewhat thick pieces of wood also lie under the arms of the magnet, and travel with them when their position is changed. These project beyond the stand A, and are used to carry the stage on which the pole pieces C rest. This stage is about 8 cm. wide and 54 cm. long; it is rather wider at one end, and here two brackets are fixed, to which the circle of the analyser D is firmly clamped so as to prevent any change of position. The polariser E is fixed at the other end of this stage; both this and the analyser are about 9 cm. from the back ends of the pole pieces. The latter have been nearly always used at a distance of 104 mm. apart, with the square ends facing each other. As slight shifting of the pole pieces takes place by frequently magnetising and demagnetising, wooden stops are screwed to the stage to prevent this; between these stops, a small carriage F runs, supporting two tubes containing the substances for examination. G is the arrangement for the sodium light; H an earthenware elbow connected with a flue to carry off the vapour from this, and products of combustion from the Bunsen burner; I the bottle of hydrogen; J the commutator, placed on a shelf under the electromagnet in a convenient position for manipulation by the observer. K K are two copper vessels which are placed on the pole pieces and supplied with a constant stream of cold water, so as to prevent, as far as possible, the temperature of the latter from being raised by conduction from the arms of the magnet. L is a brass lantern to illuminate the scale on the circle by reflection.

A frame, not shown in the above, about a metre high and two-thirds of a metre wide, is erected on the end of the table supporting the stand of the analyser. This is covered with overlapping black curtains to screen off any light from the observer, and as they overlap near the centre he is enabled to get his hand to work the analyser or to adjust the carriage carrying the tubes; the eye-piece and the glass for reading the scale pass through holes in one of the curtains. Woollen curtains, supported on a wooden frame, surround the sodium light, the end of the polariser passing through one of them. The walls of the room are also distempered black: and it is provided with a gas stove and flue, so that its temperature can be raised sufficiently high to keep easily fusible products in the fluid state.

The polariscope used for some time, consisted of the polariser and analyser of a Duboscq *saccharimètre à pénombres*, the polariser being on

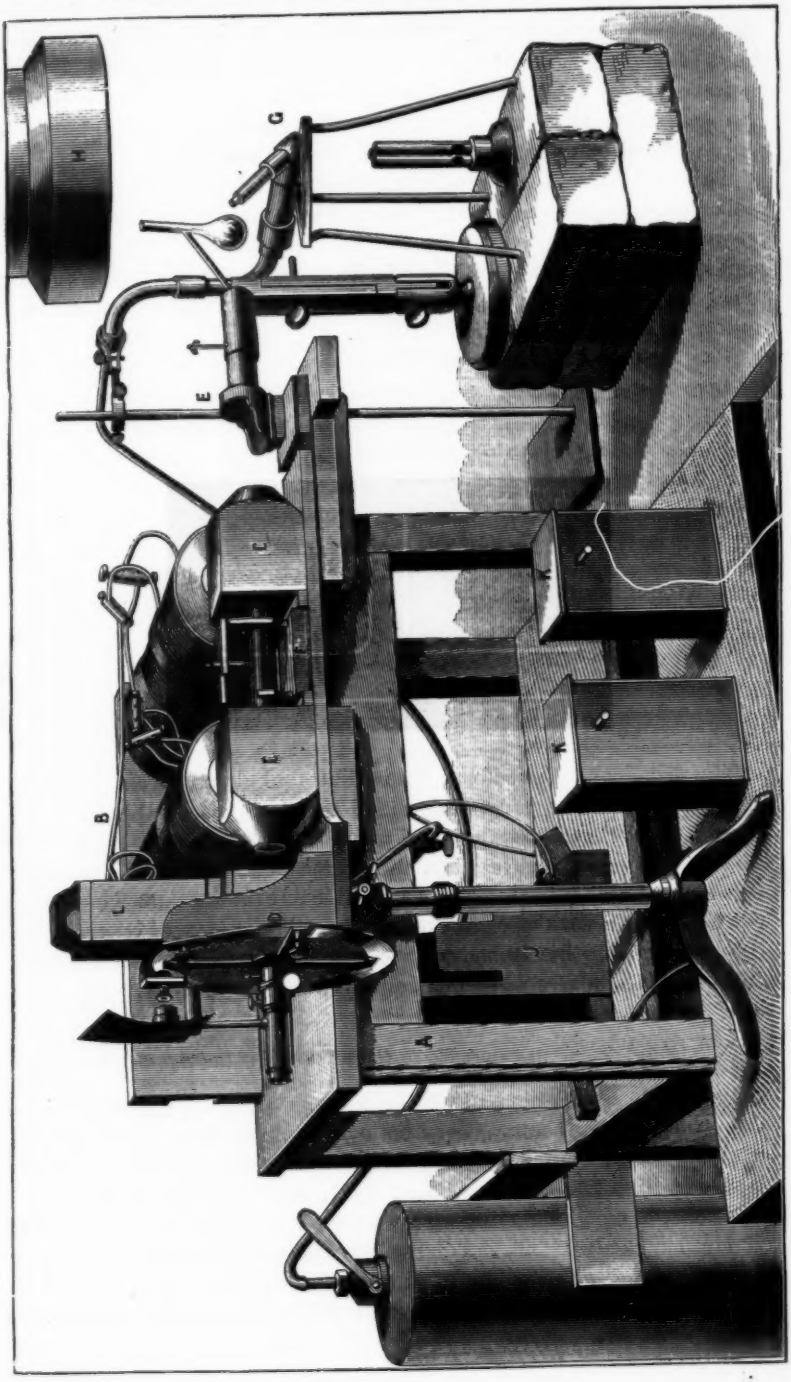


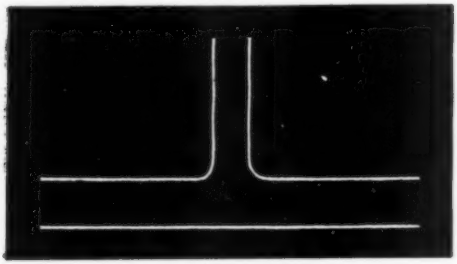
FIG. 3.

the Jellet-Cornu principle. The saccharimeter scale was also at first used (4·66 divisions = 1°), but as the divisions were found not to be quite equal, a fresh graduation was made by Hilger, one division being equal to the sixth of a degree, the vernier reading to minutes. A new Nicol prism was also inserted into the analyser.

Thinking that finer readings might be obtained by a Laurent polariser, especially as the monochromatic light at my disposal would probably allow me to employ the half quartz plate very near the parallel position, I had one made by Hilger, a large Nicol prism being used instead of a Foucault prism, and this arrangement is much preferred to the one mentioned above.

The tubes to hold the substance to be examined are of glass, and of the shape shown in the accompanying sketch.

FIG. 4.



The principal tube is about 9 mm. internal diameter and 103 mm. long, the ends being carefully ground parallel to each other; the side tube is about 6 mm. diameter and about 35 mm. long; it is used as the aperture for filling the tube by, and for taking the temperature of any substance it may contain, before and after its examination. The ground ends are closed with circles of microscope glass cemented on with glue, or, when this is unsuitable, with caoutchouc cement. Some shorter tubes than the above were also employed in special cases.

Observations in reference to the working of the Apparatus.

It has been mentioned that the distance between the pole pieces was generally 104 mm. Very little advantage arises from the use of tubes longer than can be employed in this space. This was shown by De la Rive (*Ann. Chim. Phys.*, 1871, **22**, 12), who found that a tube only 5 cm. long gave with water a rotation of 9° 15′, and one 25 cm. long only 11° 2′, the distance between the poles of the magnet corresponding with the length of the tube.

Experiments showing similar results were made with the apparatus

under consideration, and gave the following results. The measurements are only single ones, and therefore not so exact as if averages of several readings.

Distance between pole pieces and length of column of water.	Rotation, sacc. degrees.
10 mm.	18·30
20 „	19·60
30 „	20·70
40 „	21·05
50 „	21·60
75 „	22·45

So that for an increase of 65 cm. in length of column, the rise in magnetic rotation has only been 4·15, or 22·7 per cent.

Experiments were made to learn what was the condition of the magnetic field, in this apparatus, between the pole pieces when placed at different distances. The following two sets of observations are given as examples:—

I. Pole pieces 104 mm. apart, square ends facing each other. A piece of Faraday glass 9·25 mm. in thickness was placed in contact with one of the pole pieces, and then after measurement of its magnetic rotation moved to the centre of the field and again measured. The battery power used was 19·8 ampères. When against the armature it measured 14·65, and in the centre 12·85. Under these circumstances, therefore, the rotation is about 12·3 per cent. less in the centre of the field than at the sides near the pole pieces.

II. The pole pieces were placed 52 mm. apart, and the same glass measured in positions similar to the above. It gave against the pole piece 24·6, and in the centre 26·1, so that in this case a difference opposite to the above is obtained, the centre of the field giving a rotation about 6·1 per cent. greater than at the sides.

From the above experiments, it would appear probable that if the pole pieces were placed at some distance apart intermediate between 104 mm. and 52 mm., a position might be found giving a uniform field. During some recent experiments, this was very nearly attained when they were placed 77 mm. apart. It has been suggested that the lower readings obtained in Experiment II, when the glass is near the pole pieces, is due to the perforation in the pole pieces. I hope to make further experiments on this subject.

From the foregoing observations, it appeared to me that in all cases it would be desirable that the substances under examination should occupy as nearly as possible the entire distance between the pole pieces, not only to avoid loss of rotary power, but also to ensure the results being comparable, and therefore the tubes to carry them were

made as nearly that length as possible, viz., 103 mm., the ends being closed with microscope glass averaging 0·15 mm. in thickness. Under any circumstances these very thin ends are better than thicker ones, as the latter involve troublesome corrections for their own rotary power, and, unless they are all cut out of one piece of glass, separate determinations of this have to be made, whereas the correction for microscope glass of the above thickness is so small (about 0·5′) that it might almost be disregarded.

It may here be as well to speak of the difference of effect produced if the conical ends of the pole pieces face each other instead of the square ends. In most books on physics, the pole pieces described for experiments on diamagnetism have conical ends facing each other, giving the impression that in this way the magnetic force is brought to a kind of focus. The pole pieces used in the present research were made with one end square and one end conical in order to test this, and, judging from the magnetic rotation obtained, very considerable loss of power occurs by using conical ends, as the following observations show:—

I. The pole pieces were placed with their square ends facing each other and 60 mm. apart; a piece of Faraday glass was placed in the centre of the field. When magnetised, it gave a rotation of 52·0 divisions.

II. The pole pieces were placed with their conical ends facing each other and the points 60 mm. apart. The same piece of Faraday glass as the above was placed in the centre of the field, and when magnetised gave a rotation of 48·15 divisions, or about 7·4 per cent. less.

The same fact has been observed when a glass tube, full of a liquid, and occupying all the distance between the pole pieces, has been measured. In all the following experiments, the square ends have therefore been used facing each other.

Methods of Measurement. Sources of Error, &c.

When these experiments were commenced, no direct method of observing the fluctuations in the electromagnet were employed, a system of comparisons being used as by other experimenters who have worked on this subject. I have employed water as my standard of comparison. This was used by De la Rive. He called the relation of the rotation of the substance to water, taken as unity, the *specific rotation;* I have also adopted this expression. Becquerel generally employed carbon disulphide. Water, however, was preferred, although it gives a smaller rotation, as it is not liable to form convection currents, and it also changes in density very slightly for small variations in temperature. In making the measurements, two tubes of

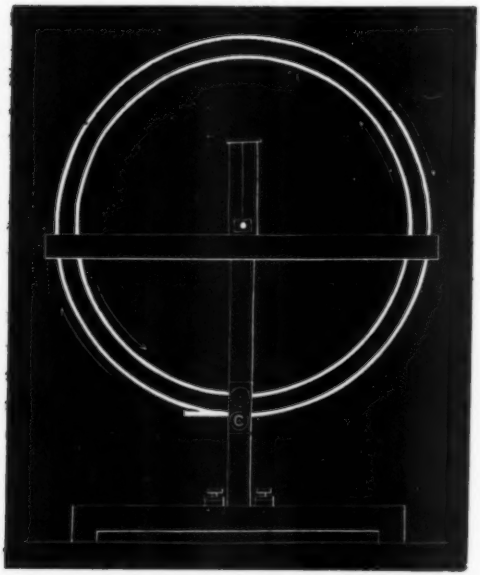
exactly the same length were used, one filled with water and one with the substance to be examined, the temperature being noted both before, and after, the set of readings (a thermometer graduated to 0·2 of a degree is now used for this purpose). The tubes were placed in the carriage, and that containing water first put into position between the two pole pieces. The current was then passed around the magnet, and the rotation measured: the current was reversed, and the opposite rotation also measured: these two numbers added together giving the double rotation of water, which is always used. This usually amounted to about 5°. Five or six double measurements of this kind were made, the series of readings being afterwards averaged. The tube containing the substance was then placed in position and measured in the same way as the water had been. The water was then again placed in position, and a second series of observations made. The mean of the two sets of water observations was considered to be the number which would have been obtained at the same time as the substance was being examined, and which would therefore be comparable. Becquerel employed this process. This method was very laborious, as two series of water readings had to be made for every one of the substance. As, however, it was found necessary to have several series of observations made with each substance, alternate readings were made, always commencing and ending with water; in this way four series of observations of the substance were made for five of water.

This method of working, however, was not considered satisfactory, and it was thought possible that, if the variations in the battery current could be registered, fewer water determinations might be necessary and greater accuracy be obtained. The difficulty, however, was to obtain a galvanometer of sufficient delicacy, and yet capable of taking a powerful current.

At first an ordinary tangent galvanometer worked on a shunt was used, but was not considered satisfactory, and it was felt that it would be desirable to have the entire current pass through the galvanometer. On mentioning my difficulties to Professor McLeod, he very kindly made two suggestions: one was to allow the entire current to pass through the ring of the tangent galvanometer, but to keep it some distance from the suspended needle, a method which has since been utilised by Sir William Thomson. The other was to use two rings of different diameters, one placed inside the other, the current being made to pass through them, but in opposite directions. The influence on the needle is then caused by the difference between them. I have worked with galvanometers of both kinds, but chiefly with the double ring one, of which a sketch is given.

The rings are made of copper wire 6 mm. thick; the inner ring is 46 cm. in diameter, the outer one about 49 cm.; this, however, is in a

Fig. 5.

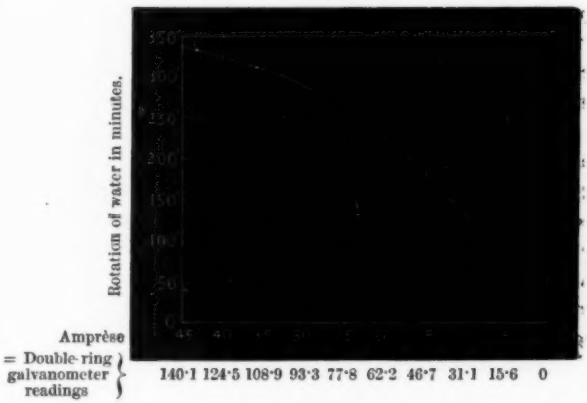


state of tension, and can be made larger or smaller, being fixed in its position by the clamp C. The needle is rather less than 2 cm. long; it is provided with a mirror, and suspended by a single cocoon thread in a square glass case. A small platinum paddle is also attached to it, which works in glycerine, and causes the needle to come rapidly to rest after being deflected. The mirror is illuminated by a lamp with an adjustable slit, and throws a sharp image on the screen. The screen is of transparent varnished cloth strained on a wooden frame 2 metres from the galvanometer, and is 2 metres long and about 10 cm. wide. It is furnished with two millimetre scales, the zero being in the centre and the scales running right and left. With the image that is obtained readings can be easily made to a millimetre. As the galvanometer is arranged, the battery power used gives a deflection of about 700 mm. on one side of the scale with the direct current, and a corresponding one on the other side with a reversed current; this amounts to a deflection of about 16° on each side.

The galvanometer is placed in a room about 9 metres from the large electromagnet. The latter has a slight influence on the galvanometer, and is arranged so that it adds to it, the amount for the direct and reversed current being about 1·2 cm. This influence of course varies with the current, so that it is not necessary to take it into account.

When this apparatus was first used, it was hoped, by carefully observing the magnetic rotation of water and the deflections of the galvanometer, that a relationship might be found so that water measurements might be dispensed with. A great number of observations were therefore made with varying battery power. Professor Ayrton kindly lent me one of his spring ammeters to compare this galvanometer with, and it showed a deflection of 126·5 cm. = 39·8 ampères. The results were plotted out on squared paper, the ordinates being the magnetic rotation of water in minutes, and the abscissæ the galvanometer readings in ampères. From Diagram I it is seen that a definite curve is formed. The portion of this curve

DIAG. I.



which corresponds to the battery power generally used is that between 135 and 110, and is practically a straight line.

After obtaining these results, the water measurements were only made, at starting a day's work, once or twice during the day, and once when concluding. But on plotting these out they did not usually follow the line of the curve as they should do, and thinking that this might be due to errors of reading, a substitute was sought for to replace the water and give higher readings, which might be calculated back to water, and thus reduce any error. Very dense glass was selected, and a strip, cut to exactly the same length as the measuring tube, was obtained from Mr. Hilger. This had a rotation of nearly six times that of water, and therefore, on reducing the readings back to the value of water, errors would be divided by that number. Unfortunately, however, these high rotations produced with highly refractive bodies cannot be measured with the same accuracy as lower ones, any imperfection in the monochromatic light influencing the tint of the

half discs. Another difficulty arises from the heavy glass not giving a homogeneous result when magnetised. This was not observed when using the first polariser *à pénombres* already referred to, although with that the readings seemed rough, but came out strongly with the Laurent polariser, ill-defined bands being seen, so that the error in these readings being greater than in ordinary cases, probably not much has been gained by the use of this glass instead of water. It was, however, used in a large amount of the work given in this paper.

A very curious observation was made which was difficult to understand, and that was that on some days the water readings were much higher, and on other days lower than the average line of the curve. It was thought that this was probably due to the action of the earth's magnetism on the galvanometer, which is extremely sensitive, and there is but little doubt that this has an injurious influence on the work, but the particular difference under consideration is evidently due to another cause. The light from the sodium flame, as already mentioned, passes through a condenser filled with dichromate solution. The sodium light is not purely monochromatic, and contains amongst other rays red rays. Solutions of potassium dichromate are not all of the same colour, and when very concentrated are much redder than when more dilute; and it was noticed that, by using a supersaturated solution (this did not deposit crystals because it was kept hot by being near to the flame), there was a great loss of light, and that the field in the polariscope was of a reddish tint. A number of measurements were made, and from the appearance of the field suspicions were aroused, and dilute dichromate used; the readings immediately increased; they were:—

	Divisions.
I. Supersaturated dichromate....	32·00
II. Dilute dichromate	32·34

These were with water. A larger result is seen from the numbers obtained with isobutyl iodide; they gave:—

	Divisions.
I. Supersaturated dichromate....	60·96
II. Dilute dichromate	62·38

As solutions of dichromate of various strengths had been used in the previous work, it is therefore believed that the variation was due to this cause. A standard solution is now always used containing 4 per cent. of dichromate, which is found to answer very well. A piece of a transparent crystal of dichromate was tried also, but from the long heating cracks formed in it.

One very unexpected source of error was found, but unfortunately not until a large amount of work had been done, a good deal of which it has rendered useless. This is the influence of the magnetic power on the optical parts of the apparatus. This does not seem to have been noticed by other workers. As Becquerel has shown, any substance placed outside the pole pieces rotates the plane of polarisation in the opposite way to that in which it would be rotated if between them. This occurs, though only to a very small extent, with the prisms, but to a larger extent with the polariser *à pénombres* than with the Laurent. It can easily be found by setting the polariscope to 0° and then making contact and measuring a few times. The effect of course increases the nearer the prisms are to the pole piece, and unfortunately during my earlier experiments no fixed position was used, therefore no definite correction can be applied to them. The influence of this correction is small in substances which have nearly the same rotation as water, the standard of comparison: but when the difference is large, as in the iodides, dibromides, &c., it is serious, throwing out their molecular rotation by 0·2 or more. The influence the polariser *à pénombres* and analyser had when in close proximity to the pole pieces was about 6′ for the double rotation; now that they are about 9 cm. from them it is about 2·5′. The word "about" is used in these cases, because the rotation varies with the strength of the current. With the Laurent prism it is only 1·4′ under the present conditions. In determining the influence of the prisms it is as well at the same time to introduce a tube with the microscope-glass ends in position, and then the measurements give the correction for both prisms and glass ends. Measurements may then be made with a smaller battery power, or it may be calculated, and a scale made which will give the value for any intermediate battery power.

The imperfections in the polarising prism may also cause errors. Noticing some peculiarities in my readings, some pieces of cocoon silk were placed across the polariser *à pénombres* so as to divide up the field into three bands. Measurements were then made on three different parts with direct and reversed currents as usual, the sums of the readings were all practically the same, but the individual readings varied, some giving higher with the direct current, and lower with the reversed, and *vice versâ*. Thus on reading on the upper and lower parts one would get results like the following:—

	I.	II.
Direct	10·5	10·9
Reversed	10·7	10·3
	21·2	21·2

and in fact, when adjusted for the upper field, careful examination shows that the bottom part is not correctly adjusted. Now, so long as the readings are made on the same part of the field, all is well; but suppose that one is made at the top and the other at the bottom, a large error will be introduced. The result would be, taking the above numbers:—

Top	10·5
Bottom.....	10·3
	20·8 = an error of ·6 or 6′.

If this were due simply to the prism being badly made it would not be worth mentioning. But I find it also exists in the Laurent form of prism, probably from some slight inequality in the thickness of the quartz plate. I have tried several of these, and they all show an inequality when measurements are made. I therefore always work with a divided field. Silk threads or cross wires do not work well if near the polariser; the eye-piece was therefore replaced by a Remsen's eye-piece with spider-lines in it, and this answers very well.

I have several times referred to convection-currents in the substance under examination as being a source of difficulty, and it certainly is a most troublesome matter, for good readings cannot be taken unless a clear image of the polariser can be obtained.

Substances vary in a remarkable way in reference to convection, the least change of temperature making some quite unmeasurable, and not affecting others; and this occurs in bodies closely related to each other. To get over this difficulty, I have filled the measuring tubes overnight and placed them in a box free from draughts, and used those first in the morning which were known to be the most likely to convect. This is an assistance, but if, by any means, any of the thin glass ends become loosened, or the glue with which they are fastened becomes cracked, products which may have cost a large amount of labour then gradually leak away and are lost.

This difficulty of convection currents I find can be overcome by modifying the optical arrangements, and, instead of having the half-quartz plate attached to the polariser, having it fastened to the analyser so that it can be focussed without having to be seen through the liquid; in this way, so long as sufficient light can be got through the fluid, it does not seem to matter how much convection is going on. Probably this will be of great value in examining products in a state of fusion, as it would be almost impossible when working at moderately high temperatures between the pole pieces to get the heating so uniform as to avoid convection.* This modification would

* Since writing the above, Mr. Glazebrook informs me that he has already used this modification of the polariscope.

probably be useful for saccharimeters, as any slight turbidity in the fluids examined would then be of little importance.

The errors of observation are another difficulty. All who have had to do work which is dependent upon the eye know too well how much depends upon the state of health of the observer, the amount of light the eye has previously been exposed to, the effect of its becoming fatigued, &c., to need much comment on this subject, except to say, that the observations required in this kind of investigation are very tiring to the eye, and on account of the numerous arrangements which have to be attended to before commencing to make observations, it is felt necessary to do as much as possible on each occasion: and usually the readings have been carried on for nine or ten hours at a time. Two observers are needed—one to register the deflections of the galvanometer, and one to read the polariscope. This work has been done by my assistant Dr. Thorne and myself.

When commencing the work of determining the molecular rotation of bodies, it was thought that, if results agreeing to about 0·1 could be obtained, nothing more would be necessary, but it soon became evident that it was necessary to work to the second place of decimals, and now, even greater accuracy than that would be liked. As it is, it is thought that, by taking the average of a great number of readings, the numbers are in most cases very nearly true to the second place: the averages for some of the substances are the results of 140 to 150, or more, eye observations.

The following is the way in which the examination has been conducted:—After the batteries have been charged and all the adjustments of the apparatus seen to, a number of measurements of heavy glass or water are made, using the direct and the reversed current alternately: the galvanometer deflections being taken for each reading. The substance to be examined, having been placed in the measuring tube some time previously or overnight, is then put in its proper position, its temperature carefully noted, and a number of readings taken. The observers then change places, and measurements are made as before. These are repeated two or three times, the observers changing each time. Again the temperature is taken, and finally the water or heavy glass is once more measured. This process is repeated with each substance. Of course the last set of heavy glass or water readings for one substance is used for the next—unless for any reason there is a cessation of work for a time.

The following is a very good example of readings: the substance examined was cetyl acetate. The readings were made on different parts of the field, hence the variation in the numbers observed.

Heavy Glass.				*Cetyl Acetate.*			
	Rotation.		Galvanometer total.		Rotation T = 22°.		Galvanometer total.
	Direct.	Reversed.			Direct.	Reversed.	
I.	87·9	87·5	124·1	II.	16·9	16·0	124·40
	88·0	87·5	123·9		16·8	16·0	124·00
					16·8	16·0	123·70
Average	175·45 = 31·97 OH_2 0·62 corr.		124·0	Average	32·83 0·62 corr.		124·03
	32·59				33·45		
				III.	16·8	16·0	123·7
VI.	86·5	87·1	121·8		16·5	16·3	123·3
	87·7	86·0	121·5		16·75	15·95	123·3
	87·5	85·9	121·4		16·45	16·0	123·3
	87·5	86·0	121·4		16·45	16·3	123·2
	173·55 = 31·62 OH_2 0·62 corr.		121·52		32·76 0·62 corr.		123·4
	32·24				33·38		
				IV.	16·5	16·4	123·2
					16·1	16·5	123·0
					17·0	15·7	122·6
					32·73 0·62 corr.		122·9
					33·35		
				V.	16·80	16·0	122·60
					16·30	16·5	122·40
					16·00	16·7	122·20
					16·65	16·0	122·20
					32·73 0·62 corr.		122·35
					33·35 T = 19°		

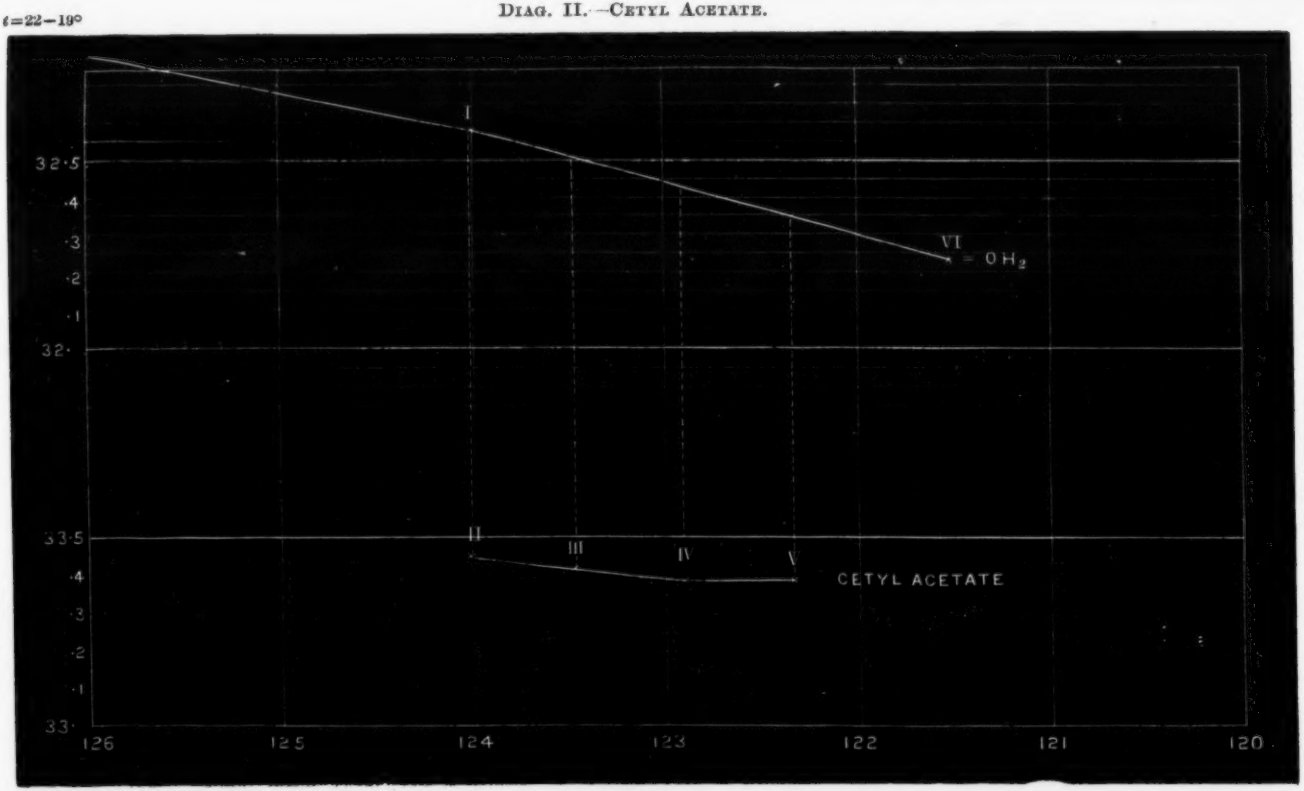
Usually not less than 5 direct and 5 reversed readings are made for each heavy glass or substance average.

The correction introduced is for the magnetic influence on the prisms.

The numbers obtained are afterwards plotted on squared paper in the following manner:—A line is drawn between the water determinations deduced from the heavy glass, and the value it gives opposite the determinations of the substance is taken as the value of water at the time the determination was made. (Diag. II.)

The above example gives the following results:—

DIAG. II.—CETYL ACETATE.



	II.	III.	IV.	V.
Cetyl acetate	33·45	33·38	33·35	33·35
Water	32·595	32·50	32·44	32·36

The change of temperature is also divided amongst the determinations, thus :—

II.	III.	IV.	V.
22°	21°	20°	19°

These results when calculated out—the density being $d\frac{21}{21} = 0{\cdot}86404$ and $d\frac{25}{25} = 0{\cdot}86120$—give the following results* :—

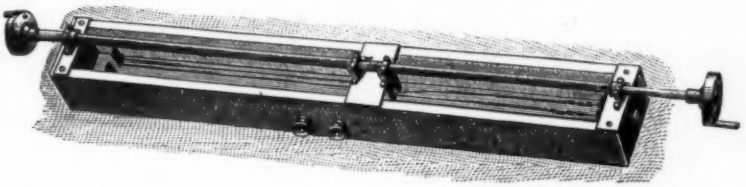
t.	Sp. rotation.	Mol. rotation.
22·0	1·0262	18·755
21·0	1·0271	18·755
20·0	1·0280	18·757
19·0	1·0306	18·789
Average 20·5	1·0280	18·764

This method entails much labour, and lately a different method has been tried which appears to be working well. It is somewhat simpler, and depends on keeping the battery current perfectly constant instead of allowing it to fall. The method of doing this is by putting in a certain amount of resistance in the circuit at starting and diminishing it as the current falls—always keeping the galvanometer index on one spot.

A resistance arrangement has been made for the purpose which answers very well. It consists of a water-tight trough about 2 feet long; in this two platinum wires (No. 20) are stretched from end to end; these are connected at one end, and at the other end terminate in binding screws to take the wires carrying the main current. As the platinum wires become heated when contact is made, the trough is kept filled with water. A piece of brass with amalgamated platinum edges is made to travel, by means of a screw, along the platinum wires and in contact with them, and shorten or lengthen the distance traversed by the current, and thus reduce or increase the resistance. (See Fig. 6.) This apparatus is placed in front of the scale and the observer watches the spot of light, and by means of a handle alters the resistance as required to keep it in one position.

* The method of calculation is illustrated by an example worked out in detail in an Appendix.

FIG. 6.



The galvanometer as usually worked is very sensitive, and all the changes in the earth's magnetism act on the needle, which is moved by only a small fraction of the current. It was therefore thought that if the needle were suspended with two threads so placed that the entire current, when passed through one ring only, would give about the same deflection as with the two rings and the needle suspended with one thread, it would be practically as sensitive to changes in the power of the current, and much less influenced by changes in the earth's magnetism. By working to one spot on each side of the scale, of course the relative value of degrees on the scale would be of no importance, though for the small angle through which the needle passes it practically follows the tangent scale. This galvanometer has been tried now for some time, and appears to act in a very satisfactory way, and hopes are still entertained of getting the arrangement so reliable that water readings may be much reduced if not dispensed with.

It may be well to state how far the errors of observations affect the results; but as these vary considerably according to the molecular weight of the bodies, no definite statement can be made. The following examples are therefore given:—

Substance.	Effect on molecular rotation of error of 1′.	
	If on substance.	If on water.
Ethyl acetate	0·017	0·014
Cetyl acetate	0·056	0·058
Ethyl crotonate	0·021	0·023
Ethyl oleate	0·060	0·068
Methyl iodide.....	0·011	0·028
Octyl iodide	0·030	0·051

Of course if any error is made in the reading of the substance and also of the standard, this effect is either compensated to some extent or augmented.

Importance of having Pure Substances to examine, and of Accuracy in determining their Density.

The purity of the substances required for the determination of physical constants is undoubtedly one of the most important points to be attended to, though at the same time to obtain them in a really pure condition is one of the most difficult things to achieve. All the substances examined in this paper have either been made in my laboratory, or, if purchased, subjected to careful purification, and in most cases it is believed that they have very closely approached a state of purity. In the fractional distillation of substances that are easily volatile, either a modification of Linnemann's dephlegmator has been used, or a simple upright distilling tube with a bulb near the top where the end of the thermometer is situated, and a lateral tube to connect it with the condenser. These tubes were about a metre long, shorter ones being used for less volatile substances. Wurtz flasks, with extra-long necks, have also been found very useful, especially for fractioning under reduced pressure. When using very long distilling tubes, it is necessary to protect them thoroughly from draughts; otherwise, it is impossible to regulate the distillation. Fractioning the chlorides of the alcohol radicals and the paraffins has been found the most troublesome, as, owing to the very low specific heat of their vapours, the indications of the thermometer are not very reliable, unless the distillation is carried on moderately fast: and yet for efficient fractioning the distillation should be slow. When distilling such bodies, it is useful to protect the region of the tube where the thermometer bulb is situated with flannel or cotton-wool.

To obtain the product perfectly anhydrous is another difficulty, and whenever the substance would bear it, phosphoric anhydride has been used. It is believed that small traces of water are absorbed by most bodies from the moisture in the air of the apparatus, and it is evident that if this be so, a substance which is fractioned a great number of times, and each time comes in contact with a fresh quantity of moist air, may absorb a good deal of water. It has often been noticed, when the density of a body has been taken after it has been distilled from phosphoric anhydride and the body redistilled without the anhydride, that on retaking its density the result will indicate that moisture has been absorbed. With bodies of high boiling point, much less difficulty is experienced in rendering them anhydrous. Like other observers, I have found sodium an unsatisfactory agent for drying alcohols, especially secondary and tertiary alcohols, the sodium compound formed apparently not being acted on by the moisture in the alcohol. Caustic baryta also has not worked well in my experiments. Anhydrous copper sulphate and caustic lime appear

to be best, but their action is slow. I have also used copper sulphate for ketones. Aldehydes are so easily changed that, as a rule, it is not safe to keep them long in contact with any dehydrating agent. Anhydrous potassium carbonate or calcium chloride has been used in these cases.

Ethyl malonate and its derivatives and also ethyl acetoacetate do not bear slow fractioning without a certain amount of decomposition taking place, and it is well to use reduced pressure. This is also true of the bromides of several of the olefines, &c.

The ethereal salts of the higher fatty acids bear distillation much better than the acids themselves, and it is considered probable that in purifying these acids, it would be best to convert them into their ethereal salts, fraction them carefully, and then saponify.

Relative Density Determinations.

When commencing the determinations of the molecular rotation of chemical substances, great difficulty was met with in trying to use the relative densities already published. First of all, they are usually given without any reference being made to the temperature of the water with which the comparison is made, and this in many cases cannot be ascertained even by consulting the original papers; secondly, many of them have been determined for one temperature only, and therefore cannot be translated for any other. Another difficulty was also experienced, and that was as to which number to take out of the many which, in some cases, are given. On this account, it was found to be necessary to take the density of all the substances before they were examined, especially as it is an important factor in the calculation of the molecular rotation. Its importance will be understood from the following example, where the influence of an error of 0·001 is taken. In ethyl acetate it will make a difference of 0·005 in its molecular rotation; in cetyl acetate 0·022, in ethyl crotonate 0·008, in ethyl oleate 0·025; in methyl iodide 0·004; and in octyl iodide 0·012, &c.; the error having a greater influence with bodies of high molecular weight and low density.

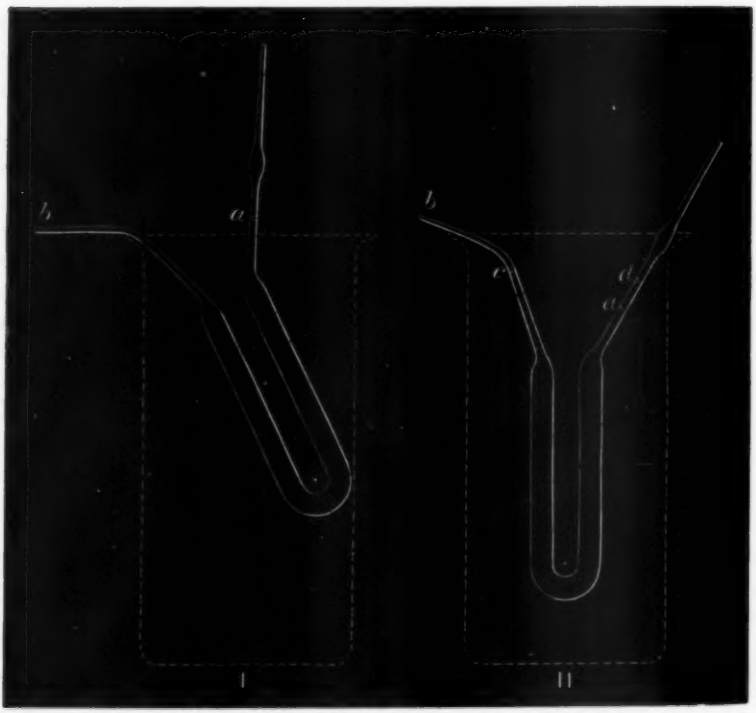
In some cases a slight impurity in the substance having a small influence on the density may not cause an appreciable error in the molecular rotation, because if it be of the same nature, as it would be if a homologous body, the variations caused in the rotation and density would more or less compensate each other.

For the determination of the densities, Sprengel **U**-tubes were at first used, but having to determine the densities of very volatile substances at temperatures sometimes considerably below that of the surrounding air, these were found to be unsuitable. With very volatile substances like pentane or aldehyde, evaporation takes place at the

capillary point of the tube, reducing the temperature so as to cause a deposition of snow at the point, and this, acting like a sponge, continually draws the fluid forward, causing a constantly increasing loss from evaporation. This may be partially prevented by the use of glass caps, but still the loss is considerable. Again, when the substance is measured at a low temperature and then allowed to warm up to that of the surrounding air, so that weighings may be made, very considerable expansion takes place and the substances occasionally overflow.

To avoid this, a modification of the Sprengel tube has been made, of such a form that immediately after the adjustment of the substance has been effected by tilting the apparatus, the liquid flows back from the point, and thus any appreciable amount of evaporation is prevented. Small vulcanised caps may then be placed on the points if necessary, and the apparatus practically sealed. Sufficient space is also left so that no overflowing from expansion occurs. The form of the apparatus will be best understood from the accompanying sketch (Fig. 7).

FIG. 7.



No. I represents it filled with the substance, the density of which is to be determined, and tilted so that the adjustment may be made.

This is done in the usual way with bibulous paper applied to the point *b*. As soon as the substance has been adjusted so as to correspond with the mark *a*, it is placed in the upright position shown in No. II. The liquid will then flow back from *b* to about *c* and *d*; the enlargement of the tube near *d* is made of sufficient dimensions to allow for any expansion of the fluid. These tubes are now used for all kinds of density determinations. They are made to hold from 5 to 10 cm.; they are always kept in boiling water some time before using. The dotted lines represent the vessel of water used for obtaining the temperature required for the determination.

In determining the density, the water in which the tube was placed was kept well agitated while the experiment was being made, and its temperature noted with a thermometer graduated to 0·02° C., and corrected at Kew. The weighings were reduced to a vacuum.*

Preparation of Substances Examined and Rotations Obtained.

PARAFFINS.

Some of these were prepared by repeatedly fractioning petroleum spirit. It was found, however, very difficult to get them in a sufficiently pure state for the study of their magnetic rotation. The difficulty chiefly arises from the iso-paraffins being associated with the normal ones, and these give higher rotations than the latter; so that, in fractioning, if the separation from the lower or higher iso-compound is imperfect, products are obtained giving too high rotations, and in the same way the iso-bodies, if contaminated with the normal, give low rotations. If the petroleum contained only one series of homologues, the impurities on each side of the fraction would of course more or less compensate each other. Thanks to the kindness of Dr. Schorlemmer, I obtained some specimens of the paraffins which he had fractioned with great care, and Dr. Thorpe also very kindly gave me a large specimen of heptane from *Pinus sabiniana*.

Pentane.

Two specimens were examined; one prepared by myself, the other by Schorlemmer. They were both distilled from phosphoric anhydride. The boiling point of the latter specimen was 36—36·5°, and a density determination gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}63373,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}62503.$$

* For formula employed, see Kohlrausch's *Leitfaden der praktischen Physik* (1880) p. 32.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
22·5°	0·8862	5·651
16·6	0·8919	5·642
10·0	0·8983	5·631
13·5	0·8964	5·647
13·5	0·8923	5·620
Average 17·2	0·8930	5·638

Isopentane.

Two specimens of this were also examined. They were distilled from phosphoric anhydride. That prepared by Schorlemmer boiled at 29—32° corr., and determinations of its density gave—

$$d\frac{15°}{15°} = 0·62479,$$

$$t\frac{25°}{25°} = 0·61590.$$

The following are the numbers obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
21·5°	0·8950	5·784
21·5	0·8882	5·740
17·0	0·8917	5·725
11·0	0·9032	5·750
11·0	0·9037	5·752
Average 16·4	0·8964	5·750

Hexane.

The specimen examined, distilled from phosphoric anhydride, boiled at 68—70° corr., and gave—

$$d\frac{15°}{15°} = 0·67392,$$

$$d\frac{25°}{25°} = 0·66619.$$

The numbers obtained for its magnetic rotation were:—

t.	Sp. rotation.	Mol. rotation.
10·5°	0·9464	6·675
11·5	0·9439	6·665
Average 11·0	0·9451	6·670

Isohexane.

Distilled from phosphoric anhydride, it boiled at 59—62° corr., and gave—

$$d\frac{15°}{15°} = 0{\cdot}66334,$$

$$d\frac{25°}{25°} = 0{\cdot}65538.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
24·0°	0·9325	6·789
19·0	0·9373	6·784
12·5	0·9394	6·750
12·5	0·9402	6·753
Average 17·0	0·9373	6·769

Heptane.

This beautiful product from *Pinus sabiniana* being regarded as a standard body, it was more thoroughly examined than the foregoing paraffins. It was distilled from phosphoric anhydride, and boiled very nearly constantly at 98·4° corr. Determinations of its density gave—

$$d\frac{15°}{15°} = 0{\cdot}68851,$$

$$d\frac{25°}{25°} = 0{\cdot}68142.$$

Dr. Thorpe found for $\frac{15°}{15°} = 0{\cdot}68838$, the substance was again distilled with phosphoric anhydride, and the density of the middle portion of the distillate determined. It gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}68850.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
13·0°	0·9507	7·656
13·0	0·9507	7·656
11·0	0·9543	7·665
12·0	0·9504	7·634
12·0	0·9490	7·634
17·0	0·9512	7·691
17·3	0·9505	7·688
17·6	0·9500	7·688
18·0	0·9481	7·675
12·3	0·9558	7·691
12·6	0·9502	7·649
12·9	0·9566	7·703
Average 14·1	0·9515	7·669

Di-isopropyl.

The specimen of this substance was very small. The density 0·668 at 0°, the only one given, had to be taken, and the expansion estimated; this of course is unsatisfactory. The tubes in which the measurements were made for the magnetic rotation were only 50 mm. long. The following are the results:—

t.	Sp. rotation.	Mol. rotation.
14·0°	0·9619	6·822
14·0	0·9548	6·772
16·0	0·9504	6·755
16·0	0·9548	6·786
Average 15·0	0·9555	6·784

Amylene—Trimethylethylene.

This substance was prepared by combining amylene boiling between 36° and 39° with hydriodic acid, removing all easily volatile products, and decomposing the iodide with alcoholic potash. The product boiled at 35—37° corr., but most of it came over at 36°. The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}67037,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}66143.$$

This is a higher density than that usually given for amylene, but that which has hitherto been examined has probably contained paraffins and isomeric amylenes.

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
17·0°	1·0447	6·077
17·5	1·0492	6·107
18·0	1·0493	6·113
10·6	1·0637	6·143
11·0	1·0634	6·145
11·4	1·0608	6·131
11·8	1·0651	6·161
11·7	1·0569	6·104
11·7	1·0569	6·104
11·7	1·0609	6·127
Average 13·2	1·0571	6·121

Chlorides.

Ethyl Chloride.

The density determinations of the substance examined gave—

$$d\frac{2^\circ}{2^\circ} = 0{\cdot}92295,$$

$$d\frac{6^\circ}{6^\circ} = 0{\cdot}91708.$$

Very few observations of the magnetic rotation of this substance could be made, owing to the mildness of the last two winters. The following results were obtained :—

t.	Sp. rotation.	Mol. rotation.
5°	1·0341	4·034
6	1·0334	4·038
6	1·0349	4·044
4	1·0348	4·031
4	1·0389	4·047
Average 5	1·0352	4·039

Propyl Chloride.

This substance was fractioned from phosphoric anhydride. It boiled at 44—45° corr. The density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}89296,$$

$$d\frac{25°}{25°} = 0{\cdot}88125.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
12·0°	1·0347	5·040
12·0	1·0334	5·033
12·0	1·0363	5·048
14·5	1·0462	5·111
15·5	1·0373	5·074
15·5	1·0374	5·073
20·0	1·0252	5·042
21·0	1·0234	5·040
22·0	1·0225	5·041
Average 16·1	1·0229	5·056

Isopropyl Chloride.

This substance was prepared from isopropyl alcohol by saturating it with hydrochloric acid, and heating the product in a sealed tube to 120°, &c. It was freed from water, and any unchanged alcohol it might contain, by distillation from phosphoric anhydride. It boiled very constantly at 35° corr. Its density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}86884,$$

$$d\frac{25°}{25°} = 0{\cdot}85750.$$

Linnemann's density, calculated for the first temperature, is $d\frac{15°}{15°} = 0{\cdot}8683$.

This substance gave the following numbers for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
18·2°	1·0228	5·157
18·2	1·0225	5·156
18·8	1 0181	5·138
18·8	1·0181	5·138
15·0	1·0302	5·173
15·0	1·0278	5·161
15·0	1·0266	5·155
15·0	1·0320	5·182
18·0	1·0240	5·162
18·5	1·0240	5·166
19·0	1·0222	5·160
Average 17·2	1·0244	5·159

Isobutyl Chloride.

This body was fractioned from phosphoric anhydride. It boiled at 68·5—69° corr. The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}88356,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}87393.$$

Linnemann obtained a rather lower density, viz., $d\frac{15^\circ}{15^\circ} = 0{\cdot}8798$.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
17·5°	1·0530	6·143
18·5	1·0504	6·134
23·5	1·0490	6·166
23·5	1·0430	6·132
23·5	1·0457	6·147
Average 21·3	1·0482	6·144

Tertiary Butyl Chloride—Trimethylcarbinyl Chloride.

This substance was obtained from Kahlbaum. It was dried with phosphoric anhydride, fractioned, and finally distilled from the anhydride. It boiled at 51—52° corr., and its density determinations gave the following numbers:—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}84712,$$

$$d\frac{25°}{25°} = 0{\cdot}83683.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
11·0°	1·0362	6·255
11·0	1·0360	6·253
16·0	1·0271	6·238
16·0	1·0340	6·280
13·8	1·0361	6·276
14·2	1·0346	6·270
17·6	1·0294	6·243
17·6	1·0306	6·250
17·6	1·0306	6·250
Average 15·0	1·0327	6·257

Isoamyl Chloride.

This was dried with phosphoric anhydride, decanted and fractioned: the specimen examined boiled at 97—99° corr. Its permanent rotation for a column 200 mm. long was only 11·6′.

The density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}88006,$$

$$d\frac{25°}{25°} = 0{\cdot}87164.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
18·0°	1·0614	7·156
18·0	1·0642	7·175
21·0	1·0597	7·166
21·0	1·0614	7·177
Average 19·5	1·0617	7·168

Tertiary Amyl Chloride—Dimethylethylcarbinyl Chloride.

This substance was prepared by the action of phosphorous chloride on dimethylethylcarbinol. It was dried with phosphoric anhydride, decanted and fractioned. The specimen examined boiled at 85—86·5° corr. The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}87086,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}86219.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
25·5°	1·0429	7·161
22·0	1·0529	7·206
22·0	1·0610	7·209
23·0	1·0475	7·174
17·6	1·0514	7·162
Average 22·0	1·0511	7·182

Octyl Chloride.

This substance was prepared by saturating octyl alcohol with hydrochloric acid, and heating the mixture at 120° in a sealed tube; the product was treated a second time in this way. The aqueous hydrochloric acid it then contained was removed, and the oil treated with phosphoric oxychloride and distilled; it was subsequently well washed with water and sodium carbonate solution, dried with anhydrous potassium carbonate, and fractioned. The specimen examined boiled at 182·5—183·5° corr., and its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}87857,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}87192.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
17·6°	1·0772	10·135
17·6	1·0775	10·138
17·6	1·0775	10·138
15·5	1·0778	10·125
16·5	1·0741	10·098
16·5	1·0763	10·118
21·6	1·0753	10·140
21·6	1·0747	10·135
Average 18·1	1·0763	10·128

Secondary Octyl Chloride.

This was prepared from the secondary alcohol in precisely the same manner as the previous body. It boiled at 171—173° corr. The determinations of its density gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}87075,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}86388.$$

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	18·0°	1·0788	10·245
	18·0	1·0822	10·278
	18·0	1·0788	10·245
	16·0	1·0787	10·229
	16·0	1·0778	10·220
	20·7	1·0795	10·274
	21·1	1·0774	10·257
	18·1	1·0778	10·247
Average	18·2	1·0769	10·248

BROMIDES.

Methyl Bromide.

A mixture of methyl alcohol with hydrobromic and sulphuric acids was employed for the preparation of this body.

It was distilled from phosphoric anhydride and boiled constantly at 4·5° corr. Its density determinations gave—

$$d\frac{0{\cdot}8^\circ}{0{\cdot}8^\circ} = 1{\cdot}73306,$$

$$d\frac{2{\cdot}2^\circ}{2{\cdot}2^\circ} = 1{\cdot}72345.$$

The first number is believed to be correct or very nearly so, and agrees pretty closely with that obtained by Merrie (*J. pr. Chem.* [2], **18**, 293), viz., 1·732 at 0°. The second determination is a little doubtful, and owing to the mildness of the last winter no opportunity has occurred to redetermine it, or to make any fresh measurements of the magnetic rotation of this bromide. The above numbers give an

expansion of 0·00686 for 1°; as this was considered too great, it was estimated from a comparison of the densities of the iodides and bromides, which gave 0·00572 for 1°. This was used in the calculations.

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
0·5°	1·5522	4·622
1·0	1·5540	4·637
1·3	1·5606	4·661
2·0	1·5520	4·646
2·5	1·5510	4·654
Average 1·5	1·5540	4·644

Ethyl Bromide.

This substance was purified by distillation from phosphoric anhydride. It boiled at 38·5—38·75° corr. Its density determinations gave—

$$d\frac{15°}{15°} = 1·44988,$$

$$d\frac{25°}{25°} = 1·43250.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
19·0°	1·3933	5·847
19·0	1·3906	5·835
19·0	1·3941	5·850
19·5	1·3986	5·873
20·0	1·3883	5·832
20·0	1·3874	5·828
20·5	1·3962	5·870
21·0	1·3957	5·872
Average 19·7	1·3948	5·851

Propyl Bromide.

Dried with phosphoric anhydride this substance boiled at 70·8—71° corr. The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}36110,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}34739.$$

Brühl's density gave $d\frac{15^\circ}{15^\circ} = 1{\cdot}36123$.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
18·5°	1·3688	6·896
19·0	1·3659	6·885
19·0	1·3646	6·879
19·5	1·3658	6·888
20·0	1·3632	6·878
Average 19·2	1·3657	6·885

Isopropyl Bromide.

This substance was fractioned from phosphoric anhydride. The specimen used boiled at 59° corr. Density determinations were made and gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}31978,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}30522.$$

Linnemann's determinations gave $d\frac{15^\circ}{15^\circ} = 1{\cdot}3172$, Bruhl's $d\frac{15^\circ}{15^\circ} = 1{\cdot}3193$.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
17·8°	1·3500	7·011
17·8	1·3491	7·006
18·6	1·3459	6·996
18·6	1·3456	6·994
15·7	1·3520	7·005
15·7	1·3523	7·007
15·7	1·3520	7·005
Average 17·1	1·3496	7·003

Isobutyl Bromide.

Dried with phosphoric anhydride and fractioned, the product examined boiled at 91·3—92·3° corr. Density determinations gave the following numbers:—

$$d\frac{15°}{15°} = 1{\cdot}27221,$$

$$d\frac{25°}{25°} = 1{\cdot}25984.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
14·0°	1·3355	7·982
14·0	1·3351	7·981
14·0	1·3371	7·995
18·5	1·3355	8·016
18·5	1·3361	8·021
18·5	1·3361	8·021
Average 16·2	1·3359	8·003

Tertiary Butyl Bromide—Trimethylcarbinyl Bromide.

This substance was prepared by saturating trimethylcarbinol with hydrobromic acid, keeping the liquid cool. After the gas had been passed for some time, a watery layer separated. The saturated product was allowed to stand for about 24 hours; it was then quickly washed with water and placed over anhydrous potassium carbonate. It was then treated with phosphoric anhydride and fractioned. The specimen examined boiled at 70·5—72·5° corr., and its density determinations gave—

$$d\frac{15°}{15°} = 1{\cdot}20200,$$

$$d\frac{25°}{25°} = 1{\cdot}18922.$$

The following numbers were obtained for its magnetic rotation:—

$t.$	Sp. rotation.	Mol. rotation.
17·5°	1·2992	8·249
18·0	1·2985	8·249
18·0	1·2985	8·249
16·0	1·2978	8·224
16·5	1·2963	8·219
17·0	1·2950	8·218
19·5	1·2959	8·245
20·0	1·2956	8·248
Average 17·8	1·2971	8·238

Isoamyl Bromide.

Purified in the same way as the preceding compound, this body boiled at 120·2—120·7° corr. The density determinations gave—

$$d\frac{15°}{15°} = 1·21927,$$

$$d\frac{25°}{25°} = 1·20834.$$

The permanent rotation was + 1·03° for a column of 200 mm. The following numbers were obtained for its magnetic rotation:—

$t.$	Sp. rotation.	Mol. rotation.
16·8°	1·3079	9·014
16·8	1·3101	9·028
16·8	1·3088	9·020
18·0	1·3162	9·081
18·0	1·3141	9·066
Average 17·3	1·3114	9·042

Octyl Bromide.

To prepare this the normal alcohol was saturated with hydrobromic acid and heated in a sealed tube at 120°. The tube was opened, the product resaturated, and again heated. After removing the aqueous layer, the oil was heated with phosphorous bromide, treated with water, then with dilute alkali, dried and distilled. The specimen examined boiled at 203—204° corr., and gave the following numbers for its density:—

$$d\frac{15°}{15°} = 1·11798,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}10993.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
19·5°	1·2458	11·986
20·0	1·2518	12·049
20·5	1·2491	12·027
21·0	1·2464	12·005
18·0	1·2520	12·033
18·0	1·2529	12·042
18·0	1·2500	12·036
Average 19·9	1·2497	12·025

Iodides.

Methyl Iodide.

This iodide was distilled with phosphoric anhydride, which is without action on it. The use of the anhydride is valuable for the purification of most of the iodides, though of course there are only a few that can be distilled with it. It not only acts as a dehydrating agent, but also removes any alcohol which may be present. Iodide of methyl purified as above boils at 42·3° corr. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 2{\cdot}28517,$$

$$d\frac{25^\circ}{25^\circ} = 2{\cdot}25288.$$

This is the highest density which has yet been found for this body.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
8·0°	2·6359	9·016
9·0	2·6369	9·026
15·0	2·6084	9·008
19·6	2·5947	9·005
24·0	2·5844	9·037
25·5	2·5607	8·973
27·5	2·5600	8·996
27·5	2·5639	9·010
Average 19·5	2·5556	9·009

Ethyl Iodide.

Dried with phosphoric anhydride, the substance boiled at 72·3—72·5° corr., and its density determinations gave the following numbers:—

$$d\frac{4°}{4°} = 1·96527,$$

$$d\frac{15°}{15°} = 1·94332,$$

$$d\frac{25°}{25°} = 1·92431.$$

Linnemann found 1·9444 at 14·5° = $d\frac{15°}{15°}$ 1·9434.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
13·8°	2·2625	10·078
13·8	2·2674	10·099
13·8	2·2638	10·084
15·0	2·2563	10·062
15·5	2·2547	10·105
16·0	2·2635	10·104
25·0	2·2295	10·040
25·0	2·2312	10·049
25·0	2·2320	10·052
Average 18·1	2·2512	10·075

Propyl Iodide.

This substance was dried with phosphoric anhydride and repeatedly fractioned; it boiled at 102—103° corr., and its density determinations gave—

$$d\frac{10°}{10°} = 1·76732,$$

$$d\frac{15°}{15°} = 1·75853,$$

The following numbers are those of other observers calculated to the same temperature:—

Linnemann (*Annalen*, **160**, 240), $d\frac{15°}{15°} = 1·74896$,

Brühl (*Annalen*, **203**, 15), „ = 1·75455,

Brown (*Chem. Soc. J.*, 1877, 22), „ = 1·7598.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
10·5°	2·0740	11·089
10·5	2·0704	11·069
15·3	2·0537	11·059
15·5	2·0654	11·099
15·5	2·0594	11·067
16·5	2·0628	11·090
16·5	2·0662	11·114
20·0	2·0490	11·056
26·0	2·0404	11·079
27·0	2·0435	11·108
27·0	2·0336	11·054
Average 18·1	2·0562	11·080

Isopropyl Iodide.

This substance was obtained from Kahlbaum. It was carefully fractioned to remove traces of allyl iodide, dried with phosphoric anhydride, and again fractioned. It boiled at 89—89·5° corr., and its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}71630,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}70049.$$

Other observers obtained—

Linnemann (*Annalen*, **161**, 50), $d\frac{15^\circ}{15^\circ} = 1{\cdot}7109$,

Brühl (*Annalen*, **203**, 15), „ = 1·7142,

Brown (*Proc. Roy. Soc.*, **26**, 245), „ = 1·71640,

„ $d\frac{25^\circ}{25^\circ} = 1{\cdot}70047$.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
23·0°	2·0098	11·162
26·0	2·0221	11·189
26·5	2·0091	11·174
27·0	2·0108	11·186
27·5	2·0104	11·178
28·0	2·0121	11·206
Average 26·3	2·0124	11·182

Isobutyl Iodide.

This substance was prepared from isobutyl alcohol by saturating it with hydriodic acid. It was washed with water and then with dilute alkali, dried over calcium chloride, and fractioned. It was then treated with phosphoric anhydride, decanted from it, and further fractioned. The specimen examined boiled at 120—121° corr. For the sake of getting it perfectly colourless, it was fractioned under reduced pressure (250 mm.), and boiled under these conditions at 83—83·25°. The density determinations gave—

$$d\frac{15°}{15°} = 1{\cdot}61385,$$

$$d\frac{25°}{25°} = 1{\cdot}6006C.$$

The following observers found—

Linnemann (*Annalen*, **160**, 240; **192**, 69), $d\frac{15°}{15°} = 1{\cdot}6140$,

Brühl (*Annalen*, **203**, 21), „ $= 1{\cdot}6150$.

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	25·0°	1·9086	12·187
	21·0	1·9141	12·183
	15·2	1·9265	12·204
	16·4	1·9275	12·224
Average	19·4	1·9192	12·199

Isoamyl Iodide.

This iodide was fractioned, dried with phosphoric anhydride, and again fractioned; it boiled at 148·25° corr. Its density determinations gave—

$$d\frac{15°}{15°} = 1{\cdot}51000,$$

$$d\frac{25°}{25°} = 1{\cdot}49811.$$

Mendelejew found 1·5087 for 15·8° $= d\frac{15°}{15°}$ 1·5102. This iodide had a permanent rotation of +1·92° for the D ray for a column 200 mm. long.

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	28·0°	1·7884	13·155
	18·0	1·8133	13·240
	18·0	1·8139	13·245
	18·0	1·8151	13·254
	16·2	1·7976	13·107
Average	19·6	1·8057	13·200

Secondary Hexyl Iodide.

This substance was dried with phosphoric anhydride and repeatedly fractioned under reduced pressure. The portion selected for examination boiled at 125·75—126·5° under 220 mm., the column of the thermometer being in the vapour. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}42694,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}41631.$$

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	22·0°	1·7173	14·249
	22·0	1·7161	14·238
	25·0	1·7090	14·211
	25·0	1·7123	14·239
	25·5	1·7077	14·206
Average	23·9	1·7125	14·229

Octyl Iodide.

This iodide was made by saturating normal octyl alcohol with hydriodic acid, and, after separating the watery layer which formed, heating the product with phosphorous iodide. It was then well washed with water and dilute alkali, dried with calcium chloride, treated with phosphoric anhydride, decanted, and fractioned under reduced pressure, *i.e.*, 330 mm. The product examined boiled at 192—194° under this pressure, the mercury column being in the vapour. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}34069,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}33163.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
19·2°	1·6242	16·200
19·3	1·6253	16·213
22·5	1·6194	16·187
22·0	1·6194	16·187
Average 20·7	1·6221	16·197

Methylene Iodide.

This was obtained from Kahlbaum. It was purified by agitation with mercury, drying with phosphoric anhydride, and fractioning several times under reduced pressure. It was obtained as a very pale straw-coloured oil boiling at 151—153° (thermometer column in vapour) under 330 mm. The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 3{\cdot}28528,$$

$$d\frac{25^\circ}{25^\circ} = 3{\cdot}26555.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
12·4°	4·1380	18·768
13·0	4·1657	18·857
13·4	4·1625	18·845
17·0	4·1502	18·831
17·0	4·1495	18·828
17·0	4·1502	18·832
Average 15·0	4·1527	18·827

Alcohols.

Methyl Alcohol.

Two specimens of this were examined; the first was prepared from methyl oxalate, the other was from wood-spirit. They were dried with copper sulphate, and boiled at 65·8—66° corr. Their densities were nearly the same; that from wood-spirit was slightly lower owing to more prolonged treatment with copper sulphate. The numbers obtained were—

$$d\frac{15°}{15°} = 0{\cdot}79726,$$

$$d\frac{25°}{25°} = 0{\cdot}78941.$$

The following numbers were obtained for the magnetic rotation of this alcohol:—

	t.	Sp. rotation.	Mol. rotation.
	21·0°	0·7251	1·627
	23·5	0·7239	1·629
	24·5	0·7229	1·628
	16·3	0·7423	1·657
	16·3	0·7410	1·655
	16·5	0·7364	1·645
	16·5	0·7303	1·633
	17·0	0·7365	1·646
	17·0	0·7334	1·639
Average	18·7	0·7324	1·640

Ethyl Alcohol.

This was dried with copper sulphate. It boiled at 78·5°, and the density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}79503,$$

$$d\frac{25°}{25°} = 0{\cdot}78820.$$

Regnault's density calculated for $d\frac{15°}{15°} = 0{\cdot}79434$.

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	21·0°	0·8553	2·764
	21·9	0·8578	2·774
	23·5	0·8614	2·784
	13·0	0·8653	2·777
	13·4	0·8621	2·767
	13·8	0·8692	2·791
	14·0	0·8685	2·790
	14·0	0·8700	2·795
Average	16·8	0·8637	2·780

Propyl Alcohol.

This was at first dried with caustic baryta and then distilled with sodium; it boiled at 97·5—98·5° corr. The density determinations gave—

$$d\frac{15°}{15°} = 0·80898,$$

$$d\frac{25°}{25°} = 0·80271.$$

As these numbers are higher than those of other observers, it was again treated with sodium and distilled. It then boiled at 98° corr., and gave—

$$d\frac{15°}{15°} = 0·80894,$$

$$d\frac{25°}{25°} = 0·80270.$$

It was then left in contact with copper sulphate for some weeks and again distilled, when it gave—

$$d\frac{15°}{15°} = 0·80883,$$

$$d\frac{25°}{25°} = 0·80247.$$

Linnemann gives $d\frac{15°}{15°} = 0·8066$, and as boiling point 97·4°.

My last densities were used in the calculation of the following numbers found for the molecular rotation :—

	t.	Sp. rotation.	Mol. rotation.
	21·0°	0·9124	3·777
	14·0	0·9147	3·773
	14·0	0·9139	3·764
	14·0	0·9129	3·759
	14·0	0·9129	3·759
	15·4	0·9152	3·772
	15·4	0·9167	3·779
	15·8	0·9149	3·772
	16·2	0·9119	3·761
Average	15·6	0·9139	3·768

Isopropyl Alcohol.

This substance was obtained from Kahlbaum. It was dehydrated, first by means of caustic baryta, and then by repeated distillation with small quantities of sodium. It boiled at 82·5—83·5° corr., and the determinations of its density gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}79165,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}78497.$$

As the action of sodium as a dehydrating agent, in the case of this alcohol, was not thought to be so effective as could be wished, it was left over anhydrous copper sulphate for some weeks and again distilled; the density determinations then gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}79136,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}78451.$$

Brühl's density calculated to $d\frac{15^\circ}{15^\circ} = 0{\cdot}7935$.

The following numbers were obtained for the magnetic rotation of this alcohol:—

t.	Sp. rotation.	Mol. rotation.
25·0°	0·9387	3·987
16·0	0·9583	4·039
16·0	0·9561	4·030
16·0	0·9559	4·029
16·0	0·9564	4·031
18·0	0·9506	4·014
18·0	0·9502	4·012
18·0	0·9502	4·012
Average 17·9	0·9520	4·019

Isobutyl Alcohol.

The substance used was ordinary isobutyl alcohol which was very carefully fractioned and dried, first with pieces of sodium, but afterwards it was left with anhydrous copper sulphate for some weeks. This had but a slight influence upon it and changed its density but little. It boiled at 107·6—108·3° corr., and the determinations of its density gave—

$$d\frac{15°}{15°} = 0\,80692,$$

$$d\frac{25°}{25°} = 0{\cdot}80085.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
16·0°	0·9622	4·909
17·6	0·9680	4·945
17·2	0·9656	4·931
17·2	0·9682	4·944
20·3	0·9673	4·951
Average 17·7	0·9663	4·936

Tertiary Butyl Alcohol—Trimethylcarbinol.

A quantity of this alcohol was obtained from Kahlbaum and slowly cooled; it then consisted chiefly of crystals: these were well drained, and this process was repeated a second time. The alcohol was kept in a fused state with anhydrous copper sulphate for a number of weeks and then distilled. It boiled at 81·5—82° corr., and the density determinations gave the following numbers:—

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}78356,$$

$$d\frac{35^\circ}{35^\circ} = 0{\cdot}77605.$$

Brühl's density calculated for $d\frac{25^\circ}{25^\circ} = 0{\cdot}7835$.

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
23·5°	0·9808	5·137
23·5	0·9827	5·148
23·5	0·9804	5·137
27·0	0·9758	5·128
26·0	0·9754	5·133
26·0	0·9707	5·096
25·0	0·9727	5·102
22·0	0·9743	5·097
22·0	0·9783	5·118
Average 24·3	0·9768	5·122

Isoamyl Alcohol (*Active*).

This alcohol was prepared from ordinary fusel oil by repeated fractional distillation, small quantities of sodium being used to dehydrate it. The specimen examined boiled at 130·5—131·5° corr. The following numbers were obtained for its density :—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}81499,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}80947.$$

It was again carefully fractioned, the middle portion of the distillate being taken. The density determinations gave numbers very close to the above, viz. :—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}81495,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}80911.$$

Brühl found for this substance a density, which if calculated for $d\frac{15^\circ}{15^\circ} = 0{\cdot}8147$.

The permanent rotation of my product for a column 200 mm. long was $-2{\cdot}27°$, *t.* 15°. The rotation found by Pedler for the purest active alcohol he could obtain was $-6{\cdot}8°$ for a column of 200 mm. So that this probably consisted of a mixture of about 2 parts of inactive and 1 part of active alcohol.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
25·25°	0·9890	5·940
19·0	0·9860	5·930
19·0	0·9911	5·960
19·0	0·9926	5·968
23·0	0·9855	5·946
16·0	0·9880	5·932
17·5	0·9841	5·916
17·5	0·9847	5·920
21·5	0·9875	5·951
21·5	0·9896	5·964
Average 19·9	0·9888	5·943

Isoamylic Alcohol (*Inactive*).

For the specimen of inactive alcohol I have to thank Dr. Frankland. It was some of the product prepared by Pedler in his investigations published in this Journal in 1868 (**21**, 74), and made from the less soluble of the barium sulphamylates obtained from ordinary amylic alcohol. On distillation it was found to boil constantly at 131·5° corr., on the same day and in the same apparatus as that used for the active alcohol. The density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}81353,$$

$$d\frac{25°}{25°} = 0{\cdot}80776,$$

making it slightly lower than the active alcohol examined.

It was nearly but not perfectly inactive, showing a rotation of $-9'$ for a column 200 mm. long.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
16·0°	0·9919	5·965
16·5	0·9916	5·965
17·0	0·9898	5·956
21·0	0·9887	5·968
22·5	0·9835	5·942
Average 18·6	0·9891	5·959

These five determinations were made side by side with the last five given for the active alcohol, and these latter average 5·937, which is 0·022 lower than the inactive. This difference may be accidental, but is sufficient to make it desirable to examine the pure active alcohol.

Tertiary Amyl Alcohol—Dimethylethylcarbinol.

This product was obtained from Kahlbaum. It was dried over anhydrous copper sulphate and fractioned. The product examined boiled at 101·5—102° corr., and the density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}81438,$$

$$d\frac{25°}{25°} = 0{\cdot}80689.$$

It quickly solidifies to a crystalline mass when cooled to —20°, and fuses at —12°.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
17·0°	0·9929	5·971
17·0	0·9892	5·950
21·5	0·9930	5·997
23·0	0·9921	6·000
23·0	0·9931	6·008
17·5	0·9931	5·976
17·5	0·9961	5·993
17·5	0·9970	6·000
Average 19·2	0·9933	5·987

Heptyl Alcohol.

This body was prepared from œnanthaldehyde, according to the directions given by Cross (*Chem. Soc. J.*, 1877, **32**, 124), namely, by

treating the aldehyde dissolved in acetic acid with successive portions of sodium amalgam for about 10 days. It was found that a good deal of œnanthylic acid was contained in the caustic alkali which was used to purify the crude alcohol obtained by this method. The alcohol boiled at 175—177° corr. The density determinations gave:—

$$d\frac{15°}{15°} = 0{\cdot}83076,$$

$$d\frac{25°}{25°} = 0{\cdot}82523.$$

The boiling point observed by Cross was 175°, and his density calculated for $d\frac{15°}{15°} = 0{\cdot}83055$.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
11·0°	1·0162	7·862
11·0	1·0181	7·877
11·2	1·0134	7·842
11·4	1·0115	7·830
11·8	1·0154	7·861
12·0	1·0145	7·855
15·0	1·0112	7·844
15·0	1·0110	7·842
15·0	1·0108	7·841
Average 12·6	1·0135	7·850

Octyl Alcohol.

This alcohol, prepared from the essential oil of *Heracleum spondylium*, was fractioned several times, and the portion boiling between 195° and 195·5° corr. taken for examination. The determinations of its density gave—

$$d\frac{15°}{15°} = 0{\cdot}83025,$$

$$d\frac{25°}{25°} = 0{\cdot}82517.$$

As the density is slightly lower than that of heptylic alcohol prepared from œnanthol, it was thought that it might possibly be impure; it was therefore converted into the acetate by digestion with acetic anhydride, and the product fractioned. The acetate boiling within 2° was then saponified with alcoholic potash, and the resulting alcohol

distilled. It boiled at 195—196° corr., and its density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}83007,$$

$$d\frac{25°}{25°} = 0{\cdot}82490.$$

This treatment therefore had but little influence upon the density, and the original product was comparatively pure.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
21·5°	1·0227	8·935
22·0	1·0199	8·913
22·5	1·0154	8·877
18·5	1·0165	8·864
18·5	1·0159	8·859
18·5	1·0146	8·848
18·5	1·0165	8·864
Average 20·0	1·0174	8·880

Secondary Octyl Alcohol.

Two specimens of this alcohol were examined: one was lent to me by Prof. Schorlemmer; the other was from Kahlbaum. This latter was fractioned, and the portion boiling at 179·5° corr. taken. The density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}82364,$$

$$d\frac{25°}{25°} = 0{\cdot}81781.$$

Brühl's numbers calculated for $d\frac{15°}{15°} = 0{\cdot}8236$.

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	13·5°	1·0264	8·997
	13·5	1·0260	8·987
	13·5	1·0261	8·988
	13·5	1·0273	8·999
	14·0	1·0242	8·974
	10·3	1·0332	9·030
	10·3	1·0329	9·027
	10·3	1·0317	9·017
Average	12·4	1·0385	9·004

Ethyl Oxide.

The specimen used was prepared from pure alcohol and rectified over phosphoric anhydride. It boiled constantly at 34·6° corr.

Its density determinations gave the following numbers:—

$$d\frac{15°}{15°} = 0·72008,$$

$$d\frac{25°}{25°} = 0·70991.$$

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	20·5°	0·8244	4·746
	20·5	0·8237	4·743
	20·5	0·8316	4·790
	22·5	0·8306	4·794
	22·5	0·8306	4·794
	18·3	0·8320	4·772
	18·3	0·8370	4·801
	18·3	0·8291	4·756
	18·3	0·8367	4·800
Average	20·0	0·8306	4·777

Isoamyl Oxide.

This substance was obtained from Kahlbaum. It was fractioned several times. The specimen selected for examination boiled at 172·5—173° corr. The density determinations gave—

$$d\frac{15°}{15°} = 0·78073,$$

$$d\frac{25^\circ}{26^\circ} = 0{\cdot}77408.$$

It was perfectly inactive.

The following numbers were obtained for the magnetic rotation of this body:—

t.	Sp. rotation.	Mol. rotation.
15·6°	0·9928	11·167
15·6	0·9928	11·167
15·5	0·9944	11·184
15·5	0·9938	11·178
16·0	0·9903	11·144
Average 15·6	0·9928	11·168

Aldehydes.

Acetaldehyde.

This was obtained from Hopkin and Williams. It was shaken with calcium chloride for a few minutes, filtered and fractioned, a fractioning tube about 1 metre long being employed. The product examined boiled at 21—22° corr., and its density determinations, taken directly after it had been distilled, gave—

$$d\frac{10^\circ}{10^\circ} = 0{\cdot}79509,$$

$$d\frac{13^\circ}{13^\circ} = 0{\cdot}79138,$$

$$d\frac{16^\circ}{16^\circ} = 0{\cdot}78761.$$

The following numbers were obtained, with freshly distilled products, for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
15·0°	0·7680	2·380
15·0	0·7679	2·380
15·0	0·7643	2·369
17·5	0·7712	2·400
17·5	0·7679	2·390
18·0	0·7677	2·392
Average 16·3	0·7678	2·385

Propaldehyde.

This was dried with calcium chloride for a short time, and fractioned. It boiled at 47—49° corr. The determinations of its density gave—

$$d\frac{15°}{15°} = 0{\cdot}80648,$$

$$d\frac{25°}{25°} = 0{\cdot}79664.$$

Rossi's density, calculated for $d\frac{15°}{15°} = 0{\cdot}806$ (*Annalen*, **159**, 79), and Pierre and Puchot give $d\frac{25°}{25°} = 0{\cdot}7972$; Brühl's numbers give $d\frac{15°}{15°} = 0{\cdot}8129$.

This substance, freshly distilled, gave the following numbers for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
14·4°	0·8424	3·363
14·4	0·8279	3·305
14·4	0·8375	3·338
14·1	0·8329	3·324
14·1	0·8421	3·361
12·25	0·8357	3·327
12·75	0·8317	3·315
12·75	0·8302	3·309
13·3	0·8394	3·346
Average 13·6	0·8355	3·332

Isobutaldehyde.

This was obtained by the oxidation of isobutyl alcohol, the product being quickly dried with calcium chloride and fractioned. It boiled at 63—64° corr., and its density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}79722,$$

$$d\frac{25°}{25°} = 0{\cdot}78787.$$

Brühl's numbers yield $d\frac{15°}{15°} = 0{\cdot}7999$.

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	22·0°	0·8526	4·314
	24·0	0·8509	4·315
	24·0	0·8507	4·314
	14·5	0·8626	4·326
	15·5	0·8607	4·321
	16·0	0·8628	4·334
Average	19·3	0·8567	4·321

Isovaleraldehyde.

This aldehyde was dried with calcium chloride for a short time and fractioned. The specimen examined boiled at 92—94° corr. It had a permanent rotation of + 2° 39′ for a column 200 mm. long. The density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}80405,$$

$$d\frac{25°}{25°} = 0{\cdot}79607.$$

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	13·0°	0·9257	5·490
	14·0	0·9225	5·476
	14·5	0·9225	5·478
	12·4	0·9285	5·503
	13·0	0·9266	5·495
	13·6	0·9238	5·482
Average	13·4	0·9249	5·487

Œnanthaldehyde.

This was purified by fractional distillation. The specimen examined boiled at 152·2—153·2° corr. Its density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}82264,$$

$$d\frac{25°}{25°} = 0{\cdot}81578.$$

The following numbers were obtained for its magnetic rotation:—

$t.$	Sp. rotation.	Mol. rotation.
14·0°	0·9655	7·427
14·8	0·9674	7·447
14·8	0·9681	7·452
15·7	0·9617	7·410
15·8	0·9639	7·426
15·8	0·9609	7·400
16·7	0·9617	7·415
17·5	0·9623	7·426
17·8	0·9597	7·408
19·0	0·9596	7·405
Average 16·2	0·9631	7·422

Ketones.

Acetone.

This substance was purified by means of hydrogen sodium sulphite, and dried, first over calcium chloride, and then over anhydrous copper sulphate with which it was kept in contact for about three months. It boiled at 55·6—55·9° corr., and its density determinations gave the following results:—

$$d\frac{15°}{15°} = 0·79652,$$

$$d\frac{25°}{25°} = 0·78669.$$

This is lower than that usually observed, but agrees pretty closely with that of Linnemann, who obtained $d\frac{15°}{15°} = 0·7975$. Thorpe's number, calculated for this temperature, gave $d\frac{15°}{15°} = 0·80244$.

The following numbers were obtained for its magnetic rotation:—

$t.$	Sp. rotation.	Mol. rotation.
15·2°	0·8716	3·526
15·2	0·8642	3·496
15·2	0·8699	3·516
15·2	0·8691	3·516
15·2	0·8716	3·526
15·2	0·8642	3·496
15·2	0·8699	3·519
15·2	0·8691	3·516
Average 15·2	0·8687	3·514

Methylpropylketone.

This substance was obtained from Kahlbaum and purified by fractional distillation, but on determining the density it was found to be much higher than that observed by others. It was therefore converted into the compound with hydrogen sodium sulphite, which was well drained, pressed, and dried, and then decomposed. The ketone was freed from water and distilled. It boiled at 102° corr. Two sets of density determinations were made, the second one being with the product which had been kept over anhydrous copper sulphate for two or three months. They gave—

	I.	II.
$d\frac{15°}{15°}$ =	0·81238	0·81233,
$d\frac{25°}{25°}$ =	0·80447	0·80423.

Frankland and Duppa's results give $d\frac{15°}{15°} = 0·8117$.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
17·0°	0·9306	5·484
17·0	0·9335	5·501
18·0	0·9323	5·500
19·0	0·9250	5·462
14·2	0·9410	5·530
14·2	0·9404	5·527
14·8	0·9342	5·494
14·8	0·9348	5·497
Average 16·1	0·9340	5·499

Paraldehyde.

This was obtained from Kahlbaum. It was purified by being cooled slowly until about half of the product had crystallised. The crystals were drained, melted, and again treated in the above manner. Density determinations of this body gave—

$$d\frac{15°}{15°} = 0·99925,$$

$$d\frac{25°}{25°} = 0·99003.$$

Brühl's density calculated for $d\frac{15°}{15°} = 1{\cdot}0001$. The above product boiled at 103·5—103·7° corr.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
16·3°	0·9079	6·671
16·3	0·9091	6·681
18·0	0·9025	6·642
18·0	0·9049	6·659
18·0	0·9046	6·657
Average 17·3	0·9058	6·662

Acids.

Formic Acid.

This acid was obtained from Kahlbaum. It had a melting point of 8°. A determination of its density gave—

$$d\frac{15°}{15°} = 1{\cdot}2283.$$

To see if it could be still further dried, it was treated with about 10 per cent. of phosphoric anhydride. This decomposed some of it on each addition, and then dissolved; the mixture was finally distilled. The acid thus obtained boiled at 101° corr., and had a density which varied but little from that given above, viz.:—

$$d\frac{15°}{15°} = 1{\cdot}22734,$$

$$d\frac{25°}{25°} = 1{\cdot}21741.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
19·5°	0·7874	1·645
20·0	0·7907	1·653
21·0	0·7948	1·663
22·0	0·8029	1·681
21·0	0·8096	1·694
21·0	0·8036	1·681
21·0	0·8008	1·675
21·0	0·8025	1·679
Average 20·8	0·7990	1·671

Acetic Acid.

Ordinary glacial acetic acid was dried in two ways. One quantity was treated with phosphoric anhydride, and then distilled; it boiled at 118—118·5° corr., and gave $d\frac{15°}{15°} = 1·0568$.

The second quantity was treated with about 10 per cent. of phosphorous chloride and distilled, fractioned from any acetyl chloride, and then distilled with anhydrous sodium acetate to remove any hydrochloric acid. It boiled at 118—118·8°. The determinations of its density gave the following results:—

$$d\frac{15°}{15°} = 1·05704,$$

$$d\frac{25°}{25°} = 1·04792.$$

The density is practically the same as that of the first specimen, the slight increase being probably due to a trace of acetic anhydride, formed by the action of the sodium acetate on a little acetylic chloride still left in the acid. This method of drying has generally been found to give products with densities a little higher than when phosphoric anhydride is alone employed, but it has been used as a check on this latter method.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
20·5°	0·8039	2·547
22·0	0·7859	2·493
24·5	0·7918	2·491
22·5	0·8016	2·544
22·5	0·7974	2·531
22·5	0·7970	2·530
18·3	0·8000	2·530
18·3	0·8022	2·537
18·3	0·7983	2·520
Average 21·04	0·7976	2·525

Propionic Acid.

This acid was dried by the two methods just described for acetic acid. The product obtained by the process in which phosphorous chloride was used boiled at 141—142° corr., and had the densities—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}99890,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}99021.$$

The specimen dried with phosphoric anhydride, and fractioned, boiled at 141·3° corr.; its densities were—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}99816,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}98957.$$

This was again treated with phosphoric anhydride and refractioned; it boiled at the same temperature; density determinations gave the following numbers:—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}99833,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}98963.$$

Linnemann found a boiling point of 140·67°, and a density at $d\frac{19^\circ}{19^\circ} = 0{\cdot}9961$ (*Annalen*, **160**, 218); his product was dried with phosphoric anhydride. His density, calculated for $t\frac{15^\circ}{15^\circ} = 0{\cdot}9996$.

Determinations of its magnetic rotation gave the following numbers:—

t.	Sp. rotation.	Mol. rotation.
20·0°	0·8452	3·496
21·0	0·8395	3·475
22·5	0·8266	3·426
25·5	0·8304	3·451
18·1	0·8382	3·461
18·1	0·8383	3·462
18·1	0·8406	3·471
20·0	0·8381	3·466
20·0	0·8348	3·453
20·0	0·8376	3·464
Average 20·3	0·8369	3·462

Butyric Acid.

This was dried with phosphorous chloride (see acetic acid). It boiled at 161—163° corr., and gave—

$$d\frac{15°}{15°} = 0{\cdot}96704,$$

$$d\frac{25°}{25°} = 0{\cdot}95882.$$

Linnemann gives its boiling point at 162·3°, and its density at $t\frac{14°}{14°} = 0{\cdot}9580$ (*Annalen*, **160**, 228); this at $t\frac{15°}{15°}$ would be 0·9572.

Brühl gives the boiling point as 161·5—162·5° at 753·2 mm., and the density at $t\frac{20°}{4°}$ as 0·9587 (*Annalen*, **203**, 19); this at $t\frac{15°}{15°} = 0{\cdot}9655$, which is still a little less than that obtained by me.

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	18·0°	0·8823	4·472
	18·0	0·8811	4·466
	18·0	0·8844	4·482
	19·9	0·8806	4·471
	19·9	0·8800	4·468
Average	18·8	0·8817	4·472

Valeric Acid.

This was prepared from propylmalonic acid, which, when heated, splits up into carbonic anhydride and valeric acid. The operation was performed in a Würtz flask with a tall neck, the heating being moderate until the decomposition was apparently complete; it was then increased and the acid distilled over. The product thus obtained was dissolved in potash, and the solution boiled for the purpose of removing ethyl valerate, which was present. (The formation of this salt is due to the presence of a small quantity of hydrogen ethyl propylmalonate contained in the acid operated upon, produced by the action of a small quantity of alcohol in the ether used in the preparation of the propylmalonic acid.) The aqueous solution of potassium valerate was decomposed by hydrochloric acid, and the acid extracted with ether. The ethereal solution was then separated, dried over calcium chloride and distilled. The acid came over as a

colourless oil, which, when refractioned, nearly all distilled between 185·2° and 187·2° corr. Phosphoric anhydride should not be used to render it anhydrous, as it acts upon it to some extent and impairs its purity.

The determinations of its density gave—

$$d\frac{15°}{15°} = 0·94462,$$

$$d\frac{25°}{25°} = 0·93749.$$

These are very slightly lower than those obtained by Lieben and Rossi (*Annalen*, **159**, 48), who found for 20°, 0·9415.

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	16·0°	0·9241	5·548
	12·2	0·9265	5·547
	12·6	0·9266	5·549
	13·4	0·9140	5·476
	13·4	0·9160	5·489
	13·6	0·9183	5·503
	13·8	0·9144	5·481
Average	13·6	0·9200	5·513

Œnanthylic or Heptoic Acid.

This acid was prepared from œnanthaldehyde by oxidation with chromic mixture, according to the directions given by Schorlemmer (*Chem. Soc. J.* [2], **11**, 1073; *Annalen*, **170**, 141). It was dried with phosphoric anhydride. It boiled at 222·5—223·5° corr. and gave the following densities:—

$$d\frac{15°}{15°} = 0·92298,$$

$$d\frac{25°}{25°} = 0·91672.$$

As the magnetic rotation of this substance was, at first thought to be abnormal, it was purified by conversion into its barium salt, which was crystallised, and then decomposed with hydrochloric acid. After drying with phosphoric anhydride, the acid boiled at 222—222·5° corr., and gave—

$$d\frac{15°}{15°} = 0·92245,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}91602.$$

The measurements of the magnetic rotation of this substance were difficult to execute, owing to its tendency to form convection currents. A very large number of observations were made, owing to the numbers obtained appearing at first to be abnormal.

t.	Sp. rotation.	Mol. rotation.
10·0°	0·9659	7·537
12·25	0·9653	7·544
11·0	0·9682	7·560
12·0	0·9626	7·522
16·0	0·9618	7·537
21·0	0·9603	7·552
21·25	0·9626	7·570
15·4	0·9679	7·563
15·4	0·9680	7·564
15·4	0·9669	7·556
10·4	0·9661	7·540
15·9	0·9658	7·565
10·4	0·9672	7·550
14·1	0·9656	7·555
17·0	0·9639	7·558
Average 14·5	0·9652	7·552

Caprylic Acid.

This acid was obtained from Kahlbaum. It was repeatedly fractioned, and the portion boiling between 236° and 239° converted into the barium salt; this was crystallised from water, and the acid separated from it with hydrochloric acid. It was taken up with ether, and the ethereal solution dried over calcium chloride; the ether was then distilled off and the acid distilled under reduced pressure, as it was thought to undergo slight decomposition when boiled under ordinary pressure. At 338 mm. it boiled nearly constantly at 211° corr., and came over as a colourless oil. On cooling, it solidified to a crystalline mass, fusing at 15°. Zincke gives the fusing point of the acid obtained by the oxidation of normal octyl alcohol as 16·5°. The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}91275,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}90826.$$

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Zincke found somewhat higher numbers, which, calculated for $d\frac{15°}{15°}$, give 0·9165.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
17·0°	0·9749	8·543
18·0	0·9752	8·550
18·0	0·9748	8·547
19·3	0·9785	8·586
19·6	0·9748	8·556
19·6	0·9760	8·566
17·0	0·9822	8·606
17·5	0·9774	8·567
20·5	0·9757	8·567
Average 18·5	0·9766	8·565

Pelargonic or Nonylic Acid.

This acid was obtained from Kahlbaum; it required repeated fractioning, and as it appears to undergo slight decomposition by long boiling, it was not obtained in quite so pure a condition as was desired. The fraction used for the measurements boiled at 247—250° uncorr., only part of the thermometer-stem being in the vapour. When cooled, it solidified to a crystalline mass fusing at 10·5°. The synthetical acid obtained by Zincke and Franchimont from octyl cyanide fused at 12·5°.

The density determinations of the above product gave—

$$d\frac{15°}{15°} = 0·91028,$$

$$d\frac{25°}{25°} = 0·90484.$$

Zincke and Franchimont's density at 17·5°, if referred to water at 4°, would make their product have a density at $t\frac{15°}{15°}$ of 0·9090, which is somewhat lower than the above. It is probable that the true density lies between mine and that of Zincke and Franchimont.

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	16·2°	0·9942	9·594
	16·2	0·9915	9·568
	16·3	0·9946	9·598
	25·5	0·9909	9·615
	25·0	0·9872	9·577
Average	19·8	0·9917	9·590

Isobutyric Acid.

The first product examined was the ordinary acid obtained by oxidising isobutyl alcohol. It was dried with phosphorous chloride (see acetic acid), and boiled at 153—154° corr. Determinations of its density gave—

$$d\frac{15°}{15°} = 0·95490,$$

$$d\frac{25°}{25°} = 0·94995.$$

This substance gave unexpected magnetic rotations, and as it was thought that this might be due to impurity of the substance, some was prepared synthetically. For this purpose, a quantity of dimethylmalonic acid was prepared and crystallised from water until of a constant fusing point. It was thoroughly dried, and then gradually heated in a small flask, provided with a condensing tube, until carbonic anhydride ceased to be evolved. The resulting isobutyric acid boiled at 153—153·5° corr., and gave—

$$d\frac{15°}{15°} = 0·95386,$$

$$d\frac{25°}{25°} = 0·94567.$$

The synthetical acid gave magnetic rotations similar to those given by the ordinary isobutyric acid.

t.	Sp. rotation.	Mol. rotation.
15·0°	0·8686	4·452
15·0	0·8706	4·462
17·5	0·8727	4·483
17·5	0·8717	4·478
17·5	0·8719	4·479
17·5	0·8691	4·464
18·3	0·8757	4·501
18·3	0·8759	4·502
18·3	0·8770	4·508
19·5	0·8721	4·487
19·5	0·8662	4·457
19·5	0·8701	4·477
Average 17·8	0·8718	4·479

Isovaleric Acid.

This was the ordinary acid obtained by the oxidation of amylic alcohol. It was roughly fractioned, dried with phosphoric anhydride, and refractioned. The specimen used boiled at 175·5—176·5°. Density determinations gave the following numbers:—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}93355,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}92610.$$

Its permanent rotation for the yellow ray, in a tube 200 mm. long, was 4·07°. The rotation of the acid prepared by Pedler from the most active alcohol he obtained was 17·2°; so that my preparation contained only about 23·6 per cent. active acid. As noticed by others, the magnetic rotation of bodies possessing a permanent rotation is on one side in excess of the latter, and when the current is reversed it is less.

This acid gave the following numbers for the magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
16·0°	0·9304	5·652
16·0	0·9334	5·670
16·0	0·9324	5·665
17·0	0·9260	5·630
17·0	0·9297	5·653
17·0	0·9189	5·587
17·0	0·9184	5·584
Average 16·	0·9270	5·635

Ethereal Salts.

Ethyl Formate.

This salt was prepared by saturating a well-cooled mixture of glacial formic acid and ethyl alcohol with hydrochloric acid. After standing for about a day, the product was diluted with its own bulk of water and distilled from a water-bath, the condenser being supplied with iced water and the receiver also cooled with ice. The ethyl formate quickly passed over, nearly free from alcohol and hydrochloric acid; as soon as the distillation became slow, it was stopped. The distillate was placed over anhydrous potassium carbonate for a day or two and then fractioned, a column about a metre long being used: it boiled nearly constantly at 54° corr. A determination of its density gave $d\frac{15°}{15°} = 0{\cdot}92263$. As this did not agree with the results of other observers, it was very slowly fractioned, but the fractioning did not change it much in density, and the boiling point varied but a fraction of a degree. Phosphoric anhydride was then slowly added to it: this at first caused a hissing noise, but after a time this ceased. It was then distilled. The density at 15° rose to 0·92542. It was again similarly treated and re-distilled; this caused a still greater rise in density. It was now several times distilled with the phosphoric anhydride until the latter was no longer acted upon, and remained in the distilling apparatus like flour. The product then gave—

$$d\frac{15°}{15°} = 0{\cdot}92973.$$

$$d\frac{25°}{25°} = 0{\cdot}91863.$$

Again distilled with the anhydride, it gave—

$$d\frac{15°}{15°} = 0{\cdot}92972,$$

$$d\frac{25°}{25°} = 0{\cdot}91863.$$

At a later period this product was redistilled, with the anhydride, and the density taken with the modified Sprengel tube; it then gave—

$$d\frac{15°}{15°} = 0{\cdot}92987,$$

$$d\frac{25°}{25°} = 0{\cdot}91881.$$

This is believed to be the most accurate determination, and was therefore employed in the calculation of the molecular rotation of this body. The boiling point scarcely varied during the above operations, being 54·2° corr.

These densities are higher than have been observed before, the product examined by Elsässer (*Annalen*, **218**, 311), when calculated for $d\frac{15°}{15°}$, giving only 0·91974. Kopp found its density at 0° = 0·9447, which, when calculated for $d\frac{15°}{15°}$, becomes 0·9282. This is the nearest to the above which I have found recorded.

The following numbers were found for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
18·3°	0·8037	3·569
16·5	0·8078	3·579
18·5	0·8044	3·572
18·5	0·8026	3·564
18·5	0·8024	3·563
18·5	0·8010	3·557
20·3	0·8023	3·571
20·3	0·7986	3·554
20·3	0·7977	3·550
Average 18·8	0·8023	3·564

Methyl Formate.

This substance was prepared from glacial formic acid and methyl alcohol by exactly the same process as the ethyl salt; it was also found to behave with phosphoric anhydride in precisely the same manner as that substance, hissing on its first addition, but having no action upon it when pure. It was treated with this reagent until its density was practically constant. It was found to be—

$$d\frac{15°}{15°} = 0·98239,$$

$$d\frac{25°}{25°} = 0·96948.$$

This density is also higher than any other recorded; the nearest appears to be that given by Grodzki and Krämer, which is 0·9797 at 15°. Elsässer found for the product he examined $d\frac{15°}{15°} = 0·9776$, which is very low. The boiling point of methyl formate was found to be 32—32·5° corr.

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
16·5°	0·7311	2·486
16·5	0·7382	2·510
16·5	0·7323	2·490
Average 16·5	0·7335	2·495

Propyl Formate.

This body was prepared by saturating a mixture of glacial formic acid and propyl alcohol with hydrochloric acid. It was dried with phosphoric anhydride and boiled at 80·5—81·5° corr. Determinations of its density gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}90989,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}90016.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
21·5°	0·8337	4·512
21·5	0·8303	4·493
21·5	0·8322	4·504
25·0	0·8388	4·556
25·0	0·8388	4·556
25·0	0·8379	4·550
25·0	0·8407	4·566
Average 23·4	0·8360	4·534

Ethyl Acetate.

Attempts were made to obtain this compound in a pure state by fractionally distilling the ordinary commercial product, but after several attempts this was given up as unsatisfactory.*

A process for its preparation was therefore sought which should at once yield it dry and free from alcohol, ether, or other bodies having a boiling point near to it. These requirements were satisfied by

* It may be remarked here that the boiling points mostly given for this body vary so much that it was found impossible to know what to expect.

employing alcohol and an excess of acetic anhydride, as in this case the products of the reaction would be only acetic acid and ethyl acetate.

In preparing it by this process, the acetic anhydride was gradually added to boiling alcohol in a distilling apparatus with a column about 1 metre high attached to the flask. When the reaction was complete any product that had distilled over was returned and the mixture digested for some time; the heat was then increased and the distillation allowed to take place until the thermometer at the top of the column rose to about 100°.

The distillate was then repeatedly fractioned in the same kind of apparatus, and a product was soon obtained boiling from 72° to 78°; this on further fractioning yielded a liquid boiling nearly constantly at 77·5° corr. This was analysed and gave numbers very close to theory. The density determinations of this product gave—

$$d\frac{15°}{15°} = 0{\cdot}90727,$$

$$d\frac{25°}{25°} = 0{\cdot}89685.$$

It was then treated with phosphoric anhydride, decanted, and redistilled, when it yielded—

$$d\frac{15°}{15°} = 0{\cdot}90724,$$

$$d\frac{25°}{25°} = 0{\cdot}89711.$$

Linnemann prepared this substance from silver acetate and ethylic iodide (*Annalen*, **160**, 209), and obtained with it a boiling point of 77° and $d\frac{15°}{15°} = 0{\cdot}9068$. He employed phosphoric anhydride to render it anhydrous.

The small portion of product boiling a little lower, viz., between 72° and 77°, is believed to be due to the absorption of a small quantity of moisture from the air by the acetate, as its boiling point was raised by treatment with phosphoric anhydride.

Elsässer has also recently determined the density and expansion of ethyl acetate, and his results calculated for $d\frac{15°}{15°}$ give 0·90710, the boiling point of his product being 77·1°.

Ethyl acetate does not bear distilling with phosphoric anhydride so well as the formate. The distillate, however, appears to be perfectly pure, but the anhydride is discoloured and there is loss of product.

The following numbers were obtained for the magnetic rotation of the compound prepared as above:—

	t.	Sp. rotation.	Mol. rotation.
	16·5°	0·8290	4·475
	10·5	0·8317	4·460
	10·5	0·8318	4·460
	10·5	0·8311	4·456
	17·75	0·8255	4·440
	17·75	0·8309	4·480
	17·75	0·8268	4·459
Average	14·5	0·8295	4·462

Ethyl Acetoacetate.

This product was purified by fractional distillation under ordinary, and then under reduced, pressure; at 760 mm. it boiled at 180—182°, at 330 mm. 152·5—153° (column in vapour). The determinations of its density gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}03174,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}02353.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
13·5°	0·9333	6·525
13·5	0·9339	6·530
13·5	0·9318	6·515
19·0	0·9230	6·481
19·0	0·9220	6·475
19·0	0·9230	6·481
16·25	0·9278	6·501

Methyl Acetate.

This substance was prepared from methyl alcohol and acetic anhydride in a similar manner to the foregoing ethyl salt. The densities of two specimens were determined; the first boiled at 56—56·5° corr., and gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}93912,$$

$$d\frac{25°}{25°} = 0{\cdot}92788.$$

The second was treated with phosphoric anhydride and then distilled; it boiled at 57·5° corr., and gave—

$$d\frac{15°}{15°} = 0{\cdot}93975,$$

$$d\frac{25°}{25°} = 0{\cdot}92858.$$

Elsässer's density calculated for these temperatures gives—

$$d\frac{15°}{15°} = 0{\cdot}93928,$$

$$d\frac{25°}{25°} = 0{\cdot}92825.$$

The second set of determinations was employed in the calculations.

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	22°	0·7835	3·381
	22	0·7770	3·353
	22	0·7772	3·353
Average	22	0·7792	3·362

Propyl Acetate.

This was prepared from propyl alcohol and acetic anhydride like the foregoing. It was treated with phosphoric anhydride. The boiling point found was 102—103° corr., and the density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}89331,$$

$$d\frac{25°}{25°} = 0{\cdot}88398.$$

Elsässer found for his product a density which calculated for $d\frac{15°}{15°} = 0{\cdot}89373$.

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
15·0°	0·8660	5·494
17·0	0·8627	5·485
17·6	0·8643	5·498
18·0	0·8592	5·468
18·5	0·8575	5·460
13·0	0·8702	5·509
13·4	0·8649	5·478
13·8	0·8672	5·495
13·2	0·8683	5·498
13·5	0·8626	5·464
13·8	0·8689	5·506
Average 15·2	0·8647	5·487

Isobutyl Acetate.

Prepared with isobutyl alcohol and acetic anhydride, it boiled at 117° corr. and gave—

$$d\frac{15°}{15°} = 0{\cdot}87743,$$

$$d\frac{25°}{25°} = 0{\cdot}86885.$$

Elsässer's determination for his product, calculated for $d\frac{15°}{15°}$, is 0·87769.

This substance gave the following numbers for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
10·5°	0·9072	6·628
10·5	0·9076	6·631
9·8	0·9063	6·620
9·0	0·9041	6·602
10·0	0·9070	6·629
10·0	0·9068	6·628
Average 10·0	0·9065	6·623

Octyl Acetate.

Prepared from pure octyl alcohol and excess of acetic anhydride. These substances were boiled together for some hours before being

fractioned. The fractioning was conducted under reduced pressure, viz., 250 mm.; at this pressure this acetate boiled at 211·25—212° (column in vapour). The densities found were—

$$d\frac{15°}{15°} = 0{\cdot}87443,$$

$$d\frac{25°}{25°} = 0{\cdot}86776.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
15·4°	0·9722	10·628
16·0	0·9704	10·612
16·8	0·9632	10·564
Average 16·1	0·9686	10·601

Ethyl Propionate.

This compound was dried with phosphoric anhydride and fractioned; the product examined boiled at 99·5—99·8° corr., and gave densities—

$$d\frac{15°}{15°} = 0{\cdot}89579,$$

$$d\frac{25°}{25°} = 0{\cdot}88628.$$

Linnemann found for his product $t\frac{15°}{15°} = 0{\cdot}8973$ (*Annalen*, **160**, 220); Elsässer obtained a density for the substance he examined which when calculated for $t\frac{15°}{15°}$ gives 0·89669. The lower numbers are believed to be nearest the truth.

This substance gave the following numbers for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
16·5°	0·8586	5·440
17·5	0·8588	5·447
15·0	0·8640	5·466
15·0	0·8634	5·461
15·0	0·8599	5·440
15·0	0·8625	5·456
Average 15·7	0·8612	5·452

*Cetyl Acetate.**

This was prepared by boiling a mixture of cetyl alcohol (from Kahlbaum) and excess of acetic anhydride for about three days. The principal part of the acetic acid which had been formed, together with the unchanged anhydride was distilled off, the thermometer bulb being kept in the fluid and the temperature not allowed to rise above 200°. The residue was then fractioned under reduced pressure.

The portion boiling at 277—278° at 190 mm. was selected for examination; even at this pressure there appears to be a slight tendency to decomposition. This body fuses at 18·5°. The determinations of its density gave—

$$d\frac{21°}{21°} = 0{\cdot}86404,$$

$$d\frac{25°}{25°} = 0{\cdot}86120.$$

It gave the following numbers for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	22·0°	1·0262	18·755
	21·0	1·0271	18·755
	20·0	1·0280	18·757
	19·0	1·0306	18·789
	20·0	1·0290	18·774
	20·5	1·0298	18·797
	21·0	1·0292	18·793
	22·0	1·0264	18·758
Average	20·7	1·0283	18·772

Propyl Propionate.

This substance was several times treated with phosphoric anhydride and fractioned. It boiled at 122—123° corr. Density determinations were made of two specimens :—

	I.	II.	Average.
$d\frac{15°}{15°}$ =	0·88696	0·88673	0·88684,
$d\frac{25°}{25°}$ =	0·87812	0·87800	0·87806.

Linnemann's determination of the density of this substance, calcu-

* See note at end of paper (p. 578).

lated for $t\frac{15^\circ}{15^\circ} = 0{\cdot}8868$ (*Annalen*, **161**, 31). Elsässer's density gives for this temperature 0·88844 (*Annalen*, **218**, 321).

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	17·0°	0·8824	6·425
	18·0	0·8806	6·418
	18·0	0·8815	6·425
	18·0	0·8800	6·414
	21·5	0·8774	6·417
	21·5	0·8779	6·421
	24·0	0·8790	6·446
	25·0	0·8763	6·432
	25·0	0·8796	6·456
	25·0	0·8769	6·436
Average	21·3	0·8792	6·429

Secondary or Isopropyl Propionate.

This was prepared by saturating a mixture of dimethylcarbinol and propionic acid with hydrochloric acid, washing and drying the product. The final drying was with phosphoric anhydride. It was then fractioned; the specimen examined boiled at 109·5—110·5° corr. The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}87172,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}86262.$$

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	18·0°	0·8912	6·609
	18·0	0·8889	6·593
	11·0	0·8966	6·601
	11·5	0·8924	6·573
	12·0	0·8938	6·587
	12·5	0·8954	6·603
	13·0	0·8918	6·580
	14·0	0·8951	6·609
	13·8	0·8925	6·588
	14·1	0·8952	6·612
	14·4	0·8920	6·590
Average	13·85	0·8932	6·595

Ethyl Butyrate.

This was prepared by saturating a mixture of butyric acid and alcohol with hydrochloric acid, &c. It was repeatedly fractioned, and the product boiling between 121° and 121·5° corr. examined.

Elsässer gives 119·9° as the boiling point, and Linnemann 121·1° (*Annalen*, **116**, 33).

The density determinations gave the following results:—

$$d\frac{15°}{15°} = 0{\cdot}88493,$$

$$d\frac{25°}{25°} = 0{\cdot}87615.$$

Elsässer's density, calculated for $d\frac{15°}{15°} = 0{\cdot}88481$; Linnemann's is rather higher.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
17·0°	0·8849	6·457
18·0	0·8855	6·468
18·0	0·8840	6·457
13·0	0·8878	6·453
13·0	0·8877	6·452
13·0	0·8915	6·479
13·0	0·8925	6·486
18·8	0·8911	6·514
18·8	0·8917	6·518
18·8	0·8874	6·487
Average 16·1	0·8884	6·477

Methyl Butyrate.

This substance was made in an analogous way to the foregoing ethyl salt; it was dried with phosphoric anhydride and fractioned, the portion boiling at 102—103° corr. being selected for examination. Krämer and Grodzki give 102·5—103·5° as the boiling point (*Ber.*, **11**, 1358), Elsässer, 102·3° (*Annalen*, **218**, 313). Density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}90365,$$

$$d\frac{25°}{25°} = 0{\cdot}89452.$$

Elsässer's determination gives $d\frac{15^\circ}{15^\circ} = 0{\cdot}90427$.

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	16·4°	0·8577	5·386
	16·4	0·8588	5·393
	16·4	0·8569	5·381
Average	16·4	0·8578	5·387

Ethyl Isobutyrate.

This was made from ethyl alcohol and the isobutyric acid obtained by oxidising isobutyl alcohol, the mixture being saturated with hydrochloric acid. It was washed, well dried with anhydrous potassium carbonate, and repeatedly fractioned. The specimen examined boiled at 110—110·6° corr. Its density was determined as follows :—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}87580,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}86695.$$

Elsässer gives the boiling point of his preparation as 110·1°, and his density calculated for $\frac{15^\circ}{15^\circ}$ becomes 0·87568.

The numbers obtained for its magnetic rotation are as follows :—

	t.	Sp. rotation.	Mol. rotation.
	24·0°	0·8732	6·484
	24·8	0·8726	6·485
	25·3	0·8671	6·449
	18·8	0·8799	6·500
	18·8	0·8773	6·480
	18·8	0·8770	6·478
Average	21·8	0·8745	6·479

Ethyl Isovalerate.

This was prepared from ethyl alcohol and isovaleric acid obtained by oxidising ordinary isoamyl alcohol, saturating the mixture with hydrochloric acid, &c. It was fractioned a great number of times. The

specimen used boiled at 135—135·25° corr. Two sets of density determinations were made, the second being with the same product as the first, but treated with phosphoric anhydride and refractioned:—

	I.	II.	Average.
$d\frac{15°}{15°}$ =	0·87139	0·87133	0·87136,
$d\frac{25°}{25°}$ =	0·86321	0·86312	0·86316.

Elsässer gives for his specimen a boiling point of 134·3°, and his density calculated for $d\frac{15°}{15°} = 0·87262$. Pierre and Puchot give the boiling point as 135·5°.

The permanent rotation of my product was + 6·2° for a column 200 mm. long, $t = 15°$. The highest rotation observed for the ethyl salt of the active acid is that given by Pierre and Puchot (*Compt. rend.*, **76**, 1332), which is $[\alpha]_D$ 1·50° for 1 cm.

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	18·0°	0·9171	7·623
	18·0	0·9167	7·619
	15·0	0·9205	7·630
	19·5	0·9130	7·600
	19·5	0·9143	7·605
Average	18·0	0·9163	7·615

Ethyl Caproate.

The acid used for the preparation of this compound was obtained from Kahlbaum, and was prepared by fermentation: it was converted into the ethyl salt by saturating its alcoholic solution with hydrochloric acid, &c. The ethereal solution was dried with calcium chloride; the ether was then distilled off, and the residue repeatedly fractioned. The substance examined boiled at 166·5—168·5° (column in vapour). Its density determinations gave:—

$$d\frac{15°}{15°} = 0·87716,$$

$$d\frac{25°}{25°} = 0·86961.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
16·0°	0·9349	8·535
16·0	0·9298	8·488
16·0	0·9339	8·524
18·8	0·9292	8·503
18·8	0·9317	8·526
18·8	0·9265	8·478
Average 17·4	0·9310	8·509

Ethyl Œnanthate.

This was prepared by the same method as the preceding ethyl salt. Two specimens were examined: No. 1 boiled at 187—188° corr.; II boiled at 187·5—189·5° corr.; they gave the following numbers for their densities :—

	I.	II.
$d\frac{15°}{15°}$	= 0·87163	0·87199,
$d\frac{25°}{25°}$	= 0·86477	0·86487.

A large number of measurements of the magnetic rotation of this substance were made, as the results were at the time thought to be abnormal. It was a troublesome body to measure, as convection so readily set in with any slight change of temperature.

t.	Sp. rotation.	Mol. rotation.
13·7°	0·9524	9·578
12·5	0·9476	9·520
12·5	0·9474	9·517
12·5	0·9488	9·531
13·0	0·9496	9·541
13·0	0·9520	9·568
13·5	0·9446	9·498
13·5	0·9459	9·511
16·0	0·9468	9·542
16·5	0·9472	9·546
17·8	0·9491	9·576
17·8	0·9447	9·532
17·8	0·9470	9·554
17·8	0·9489	9·574
Average 14·9	0·9480	9·541

Ethyl Pelargonate.

This compound was prepared from the acid examined and previously described (p. 486). The product used boiled at 226—228°, (column in vapour). Its density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}87033,$$

$$d\frac{25°}{25°} = 0{\cdot}86407.$$

Zincke and Franchimont found a density which, if referred to water at 4°, and calculated for $d\frac{15°}{15°} = 0{\cdot}8682$. The true density probably lies between this and the one given above.

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
17·9°	0·9653	11·554
17·9	0·9657	11·554
16·9	0·9745	11·586
18·9	0·9737	11·602
18·9	0·9721	11·582
18·9	0·9695	11·551
Average 18·2	0·9701	11·571

Heptyl Œnanthate.

This substance was prepared by Cross (*Chem. Soc. J.*, **32**, 127) by acting on silver œnanthate with heptyl iodide. As this process was a troublesome one the following method was tried :—A mixture of heptyl alcohol and œnanthylic acid was made, using rather more than the theoretical quantity of the acid; this was saturated with hydrochloric acid and heated in a sealed tube at 100°. An aqueous layer soon formed at the bottom of the tube. The product was mixed with ether, washed with water and then with sodium carbonate. It was then dried over anhydrous potassium carbonate, the ether driven off, and the product fractioned. After a few distillations a large part of it was obtained boiling at 276—278° (column in vapour). The density determinations gave the following results :—

$$d\frac{15°}{15°} = 0{\cdot}86522,$$

$$d\frac{25°}{25°} = 0{\cdot}85933.$$

Cross gives 270—272° as the boiling point, but does not say whether the mercury column was in the vapour. His density is also higher, viz., 0·870 at 16°.

This substance gave the following numbers for the magnetic rotation. It was a troublesome body to examine, owing to the convection currents which rapidly set in with changes of temperature:—

t.	Sp. rotation.	Mol. rotation.
11·0°	1·0058	14·685
12·0	1·0022	14·643
12·0	1·0050	14·683
12·8	1·0012	14·635
13·0	1·0023	14·653
13·0	1·0022	14·651
14·5	1·0009	14·649
14·5	1·0006	14·641
14·9	1·0024	14·675
16·1	0·9989	14·636
17·0	0·9994	14·653
Average 13·6	1·0019	14·655

Polyhydric Alcohols and their Derivatives.

Ethylene Hydrate—Glycol.

This was prepared from the monoacetate of glycol by treatment with barium hydrate. It was then repeatedly fractioned and distilled. The specimen used boiled at 196—199° corr. Its density determinations gave—

$$d\frac{15°}{15°} = 1·11678,$$

$$d\frac{25°}{25°} = 1·11208.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
13·5°	0·9569	2·949
13·5	0·9537	2·939
13·5	0·9559	2·946
15·5	0·9545	2·944
16·0	0·9526	2·939
16·5	0·9528	2·940
17·0	0·9527	2·941
Average 15·1	0·9542	2·943

Ethylene Acetate—Glycol Acetate.

The monoacetate of glycol was first made by Atkinson's process (*Phil. Mag.* [4], **16**, 433), viz., by heating a mixture of ethylene bromide, potassium acetate and alcohol at 100° in closed vessels. The product was distilled and then boiled with an excess of acetic anhydride for some hours. It was then fractioned several times. The substance examined boiled at 190—190·5° corr.

The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}11076,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}10183.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
13·0°	0·8918	6·501
13·0	0·8888	6·476
13·0	0·8864	6·463
14·8	0·8807	6·430
15·2	0·8810	6·434
15·6	0·8834	6·453
25·0	0·8756	6·445
26·0	0·8756	6·450
26·0	0·8722	6·432
Average 18·0	0·8717	6·454

Ethylene Propionate—Glycol Propionate.

This substance was prepared by boiling a mixture of glycol and propionic anhydride for several hours, and fractionally distilling the product. The substance examined boiled at 210·5—212° corr. The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}05440,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}04566.$$

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	15·0°	0·9111	8·345
	15·0	0·9134	8·365
	15·0	0·9101	8·336
	27·0	0·8973	8·308
	27·5	0·8930	8·272
	27·5	0·8942	8·284
Average	21·2	0·9032	8·318

Pinacone.

This was prepared by carefully distilling the hydrate which was obtained from Kahlbaum. If the distillation of this compound be carried on too quickly, it is liable to boil over on account of some of the water flowing back into the boiling liquid. The anhydrous body boiled constantly at 170° corr. As it will remain in a state of superfusion for some time, its density could be taken at temperatures below its melting point. The following results were obtained :—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}96718,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}96087.$$

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	22·0°	1·0721	7·311
	22·0	1·0618	7·230
	22·0	1·0712	7·294
	22·0	1·0608	7·224
	22·0	1·0660	7·259
	22·0	1·0639	7·245
	21·0	1·0633	7·236
	21·0	1·0617	7·225
	26·5	1·0564	7·215
	26·5	1·0601	7·240
	26·5	1·0567	7·217
Average	23·0	1·0631	7·245

Dimethylacetal.

This substance was obtained from Kahlbaum. It was dried with anhydrous potassium carbonate and fractionally distilled. The specimen examined boiled at 64° corr. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}85739,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}84764.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
22·0°	0·7858	4·620
13·0	0·8036	4·675
13·4	0·7963	4·635
13·8	0·8001	4·659
Average 15·5	0·7965	4·647

Diethylacetal or Acetal.

This was dried with anhydrous potassium carbonate, and fractionally distilled: it boiled at 104—104·1° corr. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}83187,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}82334.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
21·8°	0·8767	6·957
13·7	0·8836	6·973
14·2	0·8836	6·977
14·8	0·8816	6·964
Average 16·1	0·8814	6·968

Glycerol.

This substance was obtained anhydrous by distillation; it boiled at 290—290·5° corr., scarcely any decomposition occurring. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}26241,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}25881.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
15·3°	1·0155	4·112
15·3	1·0166	4·116
15·3	1·0144	4·107
16·5	1·0167	4·118
16·5	1·0169	4·119
17·2	1·0101	4·092
Average 16·0	1·0150	4·111

Ethereal Salts of Dibasic Acids.

Ethyl Oxalate.

The specimen examined boiled at 185° corr. The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}08563,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}07609.$$

Kopp's density gives $d\frac{15^\circ}{15^\circ} = 1{\cdot}0856$ and Brühl $d\frac{15^\circ}{15^\circ} = 1{\cdot}0858$.

The following numbers were obtained for the magnetic rotation of this substance:—

t.	Sp. rotation.	Mol. rotation.
13·5°	0·8929	6·664
13·5	0·8919	6·656
11·0	0·8911	6·636
11·0	0·8965	6·677
15·0	0·8880	6·636
Average 12·8	0·8921	6·654

Ethyl Malonate.

This compound was obtained from Kahlbaum; it was carefully fractioned, and the portion selected which boiled at 197·7—198·2 corr. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}06104,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}05248.$$

The following numbers were obtained for the magnetic rotation of this body :—

t.	Sp. rotation.	Mol. rotation.
8·0°	0·8883	7·400
8·0	0·8907	7·420
8·0	0·8951	7·456
9·0	0·8907	7·425
14·0	0·8837	7·404
16·5	0·8845	7·418
17·0	0·8810	7·392
17·0	0·8826	7·406
17·0	0·8827	7·407
17·0	0·8831	7·409
19·0	0·8759	7·378
19·0	0·8791	7·405
Average 14·1	0·8848	7·410

Methyl Malonate.

This was prepared by saturating a mixture of malonic acid and methyl alcohol with hydrochloric acid gas. After standing for about 24 hours, water was added and the oily layer taken up with ether; the ethereal solution was washed with sodium carbonate to remove any acid ethereal salt, dried over anhydrous potassium carbonate, and distilled. Nearly all the following ethereal salts were treated in this manner, because if any acid salt be left in them, when distilled this decomposes and yields the ethereal salt of the corresponding monobasic acid, and thus an impurity is introduced.

The methyl malonate used boiled at 181·5° corr. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}16028,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}15110.$$

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	18·0°	0·8318	5·270
	18·0	0·8336	5·282
	18·0	0·8314	5·268
	16·2	0·8331	5·271
	16·2	0·8367	5·292
	16·2	0·8370	5·296
Average	17·1	0·8339	5·280

Substitution Derivatives of Ethyl Malonate.

These compounds were first prepared simply by the method described by Conrad (*Annalen*, **204**, 129); no further purification except that of fractional distillation being resorted to. This, however, was not found sufficient owing to the presence of small quantities of secondary products. Some of these appear to be due to the saponification, or partial saponification, of the ethyl malonate by the sodium ethylate: the saline compounds thus formed enter into reaction with the iodides used and thus produce corresponding ethers or mixed ethers. There is also usually a small quantity of some iodine compound present which is not removed by distillation. In most cases therefore the compounds, prepared as described by Conrad, have been saponified, the acid separated and then reconverted into ethereal salt. Long boiling of these compounds is injurious to them, and it is best to fraction under reduced pressure.

Ethyl Methylmalonate—Ethyl Isosuccinate.

To prepare this body, ethyl malonate was treated with sodium ethylate and methyl iodide in the ordinary way. It was fractioned, and density determinations made: they gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}02865.$$

It was then saponified; the acid separated from the resulting salt by acidifying with hydrochloric acid was then extracted with ether. As mentioned before, it is important that the ether used in this and analogous operations be free from alcohol, otherwise some of the acid is converted into the acid ethereal salt, which not only wastes the product, but renders it difficult to purify. The acid was crystallised from water, well pressed between linen, and then etherified.

The ethereal salt thus prepared boiled at 198·5—199·5° corr. Density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}02132,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}01295.$$

It will be seen that the purification of the product considerably reduced its density.

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	19·2°	0·8761	8·321
	19·2	0·8750	8·311
	19·2	0·8781	8·339
	16·3	0·8802	8·340
	16·3	0·8786	8·325
	16·3	0·8780	8·320
Average	17·7	0·8777	8·326

Ethyl Dimethylmalonate.

This was prepared according to the directions given by Conrad; it was then distilled, saponified, and the dimethylmalonic acid separated as in the preparation of the previous compound. The acid was then crystallised several times from water until of a constant fusing point, and etherified. It boiled at 196·2—196·7° corr. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}00153,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}99356.$$

The following numbers were obtained for the magnetic rotation of this body :—

	t.	Sp. rotation.	Mol. rotation.
	10·5°	0·8925	9·274
	12·3	0·8912	9·273
	12·3	0·8910	9·273
	12·7	0·8929	9·295
	12·7	0·8882	9·246
	13·5	0·8906	9·276
	14·2	0·8925	9·301
	14·5	0·8890	9·267
	18·5	0·8847	9·251
	18·5	0·8850	9·255
	18·5	0·8836	9·238
Average	14·4	0·8892	9·268

Ethyl Ethylmalonate.

This was prepared according to the directions given by Conrad (*Annalen*, **204**, 134); it boiled at 209·5—211·5° corr., and the density determination gave—

$$d\frac{15°}{15°} = 1·01395.$$

It was saponified with alcoholic potash, and after evaporating off the alcohol neutralised with hydrochloric acid. The acid was then thrown down as calcium salt by means of calcium chloride; this was drained, well pressed, and dried, and the ethereal salt prepared by suspending it in alcohol and saturating with hydrochloric acid gas.

The product thus obtained boiled between 209·5—210·5° corr. and its density determinations gave—

$$d\frac{15°}{15°} = 1·01235,$$

$$d\frac{25°}{25°} = 1·00441.$$

It will be observed that the purification in this case only slightly reduced the density. Being an ethyl derivative of an ethyl salt, it is evident, that if any sodium malonate were formed in the preparation of this body, the iodide of ethyl would act upon it and again produce an ethyl compound, and therefore the product obtained would be capable of purification by fractional distillation more perfectly than in the case of compounds in the preparation of which the iodides of other radicals are employed, and when mixed ethers may be formed as secondary products.

The following numbers were obtained for the magnetic rotation of this body:—

	t.	Sp. rotation.	Mol. rotation.
	13·2°	0·9057	9·330
	13·5	0·9019	9·291
	13·8	0·9010	9·287
	14·1	0·8996	9·274
	14·1	0·8990	9·269
	14·1	0·9020	9·299
	14·1	0·9035	9·315
	16·5	0·8959	9·254
	16·5	0·8931	9·225
	16·5	0·8956	9·251
	17·0	0·8975	9·260
	17·4	0·8963	9·249
	17·6	0·8964	9·252
	18·0	0·8955	9·246
Average	15·5	0·8988	9·272

Ethyl Diethylmalonate.

This was prepared according to the directions given by Conrad (*Annalen*, **204**, 138). It was first fractioned under reduced pressure; the fraction selected being that which boiled at 195—198° under 330 mm. (column in vapour). This was then refractioned under ordinary pressure, the portion coming over at 230—230·5° (corr.) being selected for examination. The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}99167,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}98441.$$

This substance was not further purified, as from the remarks made in reference to the mono-ethyl derivative, which equally apply to this, and the care taken in fractioning, it was thought that it could not be far from pure.

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	17·6°	0·9280	11·251
	17·6	0·9178	11·127
	17·6	0·9232	11·193
	17·6	0·9235	11·196
	20·5	0·9226	11·210
	20·5	0·9232	11·216
	20·5	0·9205	11·184
Average	18·8	0·9227	11·197

Ethyl Propylmalonate.

This compound, prepared by Conrad's process, boiled at 221—224 uncorr. Its density was $d\frac{15^\circ}{15^\circ} = 0{\cdot}9955$. It was purified by saponification and conversion into the calcium salt; the acid was then separated and etherified. When fractioned under 330 mm. the principal quantity came over at 193·5—194·5° (column in vapour). The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}99309,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}98541.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
12·8°	0·9226	10·408
12·8	0·9195	10·374
12·8	0·9185	10·362
13·5	0·9199	10·383
13·5	0·9185	10·367
13·5	0·9206	10·391
13·5	0·9225	10·413
18·0	0·9145	10·358
18·0	0·9142	10·355
18·0	0·9148	10·361
19·4	0·9114	10·335
24·5	0·9117	10·379
25·0	0·9056	10·313
25·0	0·9122	10·389
25·5	0·9091	10·357
Average 18·1	0·9152	10·367

Ethyl Isopropylmalonate.

This substance, as prepared by means of ethyl malonate, sodium ethylate and isopropyl iodide, boiled at 216·5—217·5° corr. Its density was $d\frac{15^\circ}{15^\circ} = 0{\cdot}99908$. It was saponified and converted into calcium salt, which was well pressed. The acid was then separated and etherified. The ethyl isopropylmalonate then boiled at 188—188·5° (column in vapour) under a pressure of 330 mm., and the density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}99271,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}98521.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
16·3°	0·9265	10·485
17·0	0·9245	10·467
17·5	0·9236	10·461
18·5	0·9252	10·486
22·75	0·9193	10·454
14·2	0·9292	10·498
14·2	0·9285	10·490
15·0	0·9340	10·517
16·8	0·9257	10·479
Average 16·9	0·9267	10·482

Ethyl Succinate.

This was prepared by saturating a mixture of alcohol and succinic acid with hydrochloric acid. It boiled at 216·5° corr. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}04645,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}03832.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
18·5°	0·9043	8·376
18·5	0·9041	8·373
19·5	0·9022	8·363
19·5	0·9026	8·366
19·5	0·9075	8·412
19·5	0·9013	8·355
19·5	0·9062	8·400
14·5	0·9084	8·388
14·5	0·9081	8·385
14·5	0·9080	8·384
Average 17·8	0·9053	8·380

Methyl Succinate.

This was prepared in a similar manner to that employed for the ethyl salt. It boils at 195·25° corr. Its melting point is given as 20°; my observations make it 18·5°, but it is capable of remaining liquid at a much lower temperature for a considerable time. On one occasion it remained fluid for about 14 days at a temperature below its fusing point, and when tested it was found to be 15°. The introduction of the thermometer started crystallisation very soon. It is a very beautiful substance, forming large crystals. The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}12611,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}11718.$$

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	18·0°	0·8590	6·202
	18·0	0·8666	6·257
	18·0	0·8609	6·216
	18·5	0·8641	6·242
	18·5	0·8643	6·243
Average	18·2	0·8630	6·232

Ethyl Pyrotartrate (methylsuccinate).

This ethereal salt was prepared in a similar manner to the above. It boiled at 217·5—218·5° corr. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}01885,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}01126.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
18·5°	0·9084	9·336
18·5	0·9079	9·332
18·5	0·9076	9·328
17·9	0·9130	9·380
17·0	0·9087	9·329
17·5	0·9069	9·316
14·0	0·9175	9·398
17·5	0·9118	9·364
17·8	0·9083	9·330
16·0	0·9115	9·350
17·5	0·9118	9·364
18·0	0·9085	9·334
Average 17·4	0·9102	9·347

Ethyl Acetosuccinate.

The specimen examined was given me by Dr. Thorne. It was prepared by acting on ethyl acetosodacetate with ethyl chloracetate. It boiled at 239—240° (column in vapour) under 330 mm. The density determinations gave—

$$d\frac{15°}{15°} = 1·08809,$$

$$d\frac{25°}{25°} = 1·08049.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
21·5°	0·9389	10·402
21·5	0·9297	10·300
23·5	0·9324	10·337
23·5	0·9327	10·341
23·5	0·9324	10·337
Average 22·7	0·9332	10·343

Ethyl Suberate.

The acid employed in the preparation of this substance was obtained from Schuchardt. It was etherified in the usual manner with hydrochloric acid and alcohol. The product boiled at about 282—286° under the ordinary atmospheric pressure, but as it appeared to undergo slight decomposition it was fractioned under reduced pressure. The specimen examined boiled at 251—253° (column in vapour) under 320 mm. pressure. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}98519,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}97826.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
17·5°	0·9591	12·461
17·5	0·9562	12·425
17·5	0·9594	12·465
11·0	0·9647	12·478
11·0	0·9655	12·488
11·6	0·9622	12·450
11·6	0·9650	12·458
Average 14·0	0·9617	12·461

Ethyl Sebate.

This was prepared in the same manner as the preceding ethereal salt. The sebacic acid used was obtained from Kahlbaum. The boiling point of the product examined was 307—308° corr. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}96824,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}96049.$$

It was a very troublesome product to measure on account of convection.

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
10·7°	0·9790	14·444
11·3	0·9826	14·505
11·3	0·9807	14·477
14·1	0·9793	14·488
14·5	0·9806	14·511
14·6	0·9806	14·512
14·6	0·9811	14·520
15·2	0·9789	14·495
15·5	0·9787	14·495
15·5	0·9793	14·504
15·5	0·9807	14·524
15·0	0·9777	14·474
Average 14·0	0·9799	14·496

Isobutyl Succinate.

A mixture of isobutyl alcohol and succinic acid was saturated with hydrochloric acid and allowed to stand, but as the succinic acid does not dissolve freely in the alcohol a quantity of it is not acted upon; the mixture was therefore warmed once or twice in the day, and by repeating this operation for about four or five days all the acid disappeared. Water was then added, the oily layer separated, washed with sodium carbonate, dried, and distilled. After a little fractioning it boiled at 264·75—265·75° corr. The determinations of its density gave—

$$d\frac{15°}{15°} = 0{\cdot}97374.$$

$$d\frac{25°}{25°} = 0{\cdot}96670.$$

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	13·0°	0·9706	12·718
	13·8	0·9661	12·667
	13·8	0·9691	12·706
	14·8	0·9664	12·680
	14·8	0·9698	12·724
	14·8	0·9702	12·730
	15·7	0·9673	12·700
	15·7	0·9696	12·732
Average	14·5	0·9686	12·707

BROMIDES OF OLEFINES.

Methylene Bromide.

The preparation of this substance was at first attempted by heating a mixture of methyl iodide and bromine to about 230°. (The mixture requires to be made at a temperature below 0°.) The product obtained in this way consisted of two or more bodies, and it was not found possible to get the methylene bromide sufficiently pure by this process.

The original method of Butlerow was therefore resorted to. This consists in treating methylene iodide, placed under water, with bromine, the directions lately given by Henry (*Ann. Chim. Phys.* [5], **30**, 267) being followed. The process worked satisfactorily; but to ensure the removal of all iodine from the product, it was treated

again with a small quantity of bromine. After this had been removed, it was dried with anhydrous potassium carbonate and carefully fractioned several times, a long fractioning tube being employed. The substance examined boiled between 96·5° and 98·5°. Density determinations gave—

$$d\frac{15°}{15°} = 2·49922,$$

$$d\frac{25°}{25°} = 2·47849.$$

As these numbers differed so widely from those of Henry, who obtained 2·4930 at 0°, equal to about $d\frac{15°}{15°} = 2·4417$, the substance was refractioned and distilled from phosphoric anhydride, the portion boiling at 96·5—97·5° corr. being selected for examination: this gave—

$$d\frac{15°}{15°} = 2·49850,$$

$$d\frac{25°}{25°} = 2·47745.$$

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	16·0°	2·1024	8·141
	16·5	2·1040	8·148
	17·0	2·1035	8·152
	18·0	2·1006	8·145
	14·5	2·0827	8·054
	14·5	2·0847	8·059
	14·5	2·0867	8·070
Average	15·9	2·0949	8·110

Ethylene Bromide.

This was prepared by passing ethylene, prepared from alcohol and sulphuric acid, through bromine covered with water. It was then washed with alkali, dried, and rectified. To render it purer, it was very slowly cooled, and when about half of it had crystallised, the crystals were well drained and pressed between bibulous paper. They were then melted and the fluid again slowly cooled, until about half of it had crystallised. The fluid was drained off, and this operation repeated a third time. The crystals then fused at 8·2—8·4°. The

substance was finally dried with anhydrous potassium carbonate. Three different specimens were examined: two of my own preparation, and one from the purified crystals obtained from Kahlbaum's product. They gave the following densities:—

	I.	II.	III.
$d\frac{15°}{15°}$	2·16061	2·16681	2·17507

It will be seen from these that the products were not alike.

On distilling this crystallised ethylene bromide, a very small quantity of water at first came over with it; the temperature then rose to 130°, and it nearly all came over between this and 131·5°. As it was found that this substance was unattacked by boiling with phosphoric anhydride, it was distilled from it. The temperature gradually rose to 130·5°, and the product between this and 131·5° was collected. The temperature then remained nearly stationary at 131·5°, about one-third of the original product passing over at this temperature: the density determinations of the two fractions gave—

I.	II.
130·5—131·5°	131·5°
2·17334	2·18891

It is curious to see what a large difference of density there is between these two fractions with boiling points lying so closely together.

Fraction II was again distilled from phosphoric anhydride. A little came over below 131·5° and was rejected; the remainder distilled between 131·5° and 131·75°. It gave the following results:—

$$d\frac{15°}{15°} = 2·18934,$$

$$d\frac{25°}{25°} = 2·17271.$$

A specimen of crystallised product prepared from Kahlbaum's bromide was then fractioned with phosphoric anhydride. A little came over below 131·5°. The remainder distilled between 131·3° and 131·5°: the density of this latter product was—

$$d\frac{15°}{15} = 2·18802.$$

Here the boiling point was slightly lower, and, as a consequence, the density was also slightly lower.

The two last products were mixed and refractioned without phos-

phoric anhydride. The boiling point soon rose to 131·5°, and most of the substance came over between 131·5° and 131·6°: the numbers given by this were—

$$d\frac{15°}{15°} = 2{\cdot}18859,$$

$$d\frac{25°}{25°} = 2{\cdot}17197.$$

It is thought that the average of the last three densities gives very nearly the true density of ethylene bromide. If anything, it is probably slightly low.

I	$d\frac{15°}{15°}$	2·18891
II	„	2·18934
III	„	2·18859
Average	„	2·18895

The two determinations made at 25°, when compared with the corresponding ones made at 15°, show identically the same variation in density for the 10° between 15° and 25°, viz., 0·01664. This is very close to that found by Thorpe (*Chem. Soc. J.*, 1880, 177), which is 0·01658. The density, however, is considerably higher, and corresponds closely to that found by Reboul, viz., 2·198 at 10°, the above density at that temperature becoming 2·19844. All other observers give lower densities. No examination of the products which render the bromide of ethylene impure has been made.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
12·0°	2·0325	9·678
12·0	2·0291	9·662
18·0	2·0257	9·689
18·0	2·0336	9 727
13·1	2·0396	9·719
13·1	2·0376	9·709
13·1	2·0304	9·676
17·2	2·0319	9·717
17·5	2·0298	9·707
17·8	2·0314	9·715
Average 15·2	2·0322	9·700

Ethylidene Bromide—Methylmethylene Bromide.

This substance was prepared from paraldehyde by the action of $P^5Cl_3Br_2$. On adding paraldehyde to the phosphoric trichlorodi-

bromide, a very energetic action takes place; so that it is necessary to add it by degrees. After the action was completed, the mixture was agitated with water to decompose the oxychloride of phosphorus, small quantities being added at intervals. The oil, which is very irritating to the eyes, was then distilled with water, and the oily part of the distillate separated, dried, and repeatedly fractioned. When nearly pure, it was agitated with phosphoric anhydride, filtered, and refractioned. The product used boiled at 108—110° corr. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 2{\cdot}10294,$$

$$d\frac{25^\circ}{25^\circ} = 2{\cdot}08540.$$

Both the boiling point and density is lower than that given by Tawildarow (*Annalen*, **176**, 12). The boiling point he gives is 114—115°, and the sp. gr. at 10°, 2·129.

A large number of observations were made of the magnetic rotation of this body before the influence of magnetism on the prisms was observed, and unfortunately the correction cannot be now made, as the position of the prisms used in these measurements cannot be found; the numbers obtained varied between 9·1 and 9·2, and it is believed that 9·1 is very near the truth. This has been adopted in this paper. It is proposed to prepare a fresh specimen of this substance—the last having become too small in quantity for fresh readings—so that more numbers may be obtained.

Propylene Bromide—Methylethylene Bromide.

This substance was prepared by passing propylene, obtained by heating thymol with phosphoric anhydride, into bromine covered with water. It was first purified by fractional distillation, and then by distillation with phosphoric anhydride. It boiled at 142—142·3° corr. The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}94474,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}93030.$$

Thinking that the distillation with phosphoric anhydride might have injured it, it was fractioned alone, under reduced pressure; it boiled at 121·8—122·5° under 330 mm. Its density determinations then gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}94426,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}93004.$$

Linnemann's density gives $d\frac{15^\circ}{15^\circ} = 1{\cdot}9492$.

This substance gave the following numbers for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	13·0°	1·8779	10·823
	13·0	1·8778	10·823
	17·1	1·8727	10·826
	17·2	1·8689	10·802
	15·0	1·8756	10·827
Average	15·1	1·8746	10·820

Dimethylmethylene Bromide—Bromacetol.

This substance was prepared by the process of Reboul (*Ann. Chim. Phys.* [5], **14**, 479). The mixture of bromides resulting from the union of hydrobromic acid with ordinary bromopropylene was fractioned, and the part boiling between 115—130° was then treated with alcoholic potash, &c. Unfortunately the quantity obtained was small. It boiled at 114—116°, and its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}84761,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}83140.$$

The following numbers were obtained for its magnetic rotation. The amount of substance being small, it had to be measured in a tube only 35 mm. long:—

	t.	Sp. rotation.	Mol. rotation.
	20·8°	1·6664	10·176
	20·0	1·6627	10·145
	20·5	1·6565	10·110
	21·5	1·6561	10·117
Average	20·7	1·6604	10·137

Trimethylene Bromide.

This substance was purified by fractional distillation. The portion selected for examination boiled at 165·5—167° corr., at 743 mm. It was refractioned under reduced pressure, and boiled at 135·5—136·5° (column in vapour), under 330 mm. The density determinations gave—

$$d\frac{15°}{15°} = 1·98236,$$

$$d\frac{25°}{25°} = 1·96836.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
19·0°	1·8191	10·303
19·5	1·8201	10·336
19·0	1·8210	10·338
21·0	1·8180	10·336
23·5	1·8200	10·366
24·0	1·8070	10·299
24·0	1·8220	10·383
13·2	1·8300	10·346
13·2	1·8325	10·361
Average 19·6	1·8211	10·341

Isobutylene Bromide—Dimethylethylene Bromide.

This substance was obtained from Kahlbaum. It was fractioned several times, and the portion boiling between 147—150° collected for examination. The density determinations gave—

$$d\frac{15°}{15°} = 1·74343,$$

$$d\frac{25°}{25°} = 1·73083.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mot. rotation.
16·5°	1·7163	11·826
16·5	1·7214	11·861
16·5	1·7199	11·851
12·6	1·7363	11·932
12·6	1·7375	11·940
12·6	1·7360	11·930
Average 14·5	1·7279	11·890

Isobutylene bromide undergoes slight decomposition when distilled. After the above experiments were made the product was refractioned under 313 mm. pressure: it then boiled at 118—120°. Its density was considerably altered by this treatment, and was—

$$d\frac{15°}{15°} = 1·75586,$$

$$d\frac{25°}{25°} = 1·74294.$$

The above numbers could not be calculated with this density, as the product, having altered, would therefore also give different readings if re-examined. It is, however, thought that the molecular rotation found is not far from the truth, on account of the position it occupies in relation to propylene and amylene bromides. Any impurity in the product which would reduce the density would also reduce the specific rotation, and thus compensation would take place to a certain extent. The last density forms a better curve with the other dibromides of this series than the former one.

Isoamylene Bromide—Trimethylethylene Bromide.

In the preparation of this substance, amylene boiling between 36° and 39° was used. It was cooled in a freezing mixture, and bromine gradually added to it; the operation did not go on very regularly. The crude bromide was washed with dilute alkali, and then with water, and dried over anhydrous potassium carbonate. It was fractioned under reduced pressure, and then gave—

$$d\frac{15°}{15°} = 1·64000,$$

$$d\frac{25°}{25°} = 1·62921.$$

Refractioned under 215 mm. it boiled at 126—127·5°, and its density determinations gave—

$$d\frac{15°}{15°} = 1·63699,$$

$$d\frac{25°}{25°} = 1·62595.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
10·4°	1·6628	12·941
11·2	1·6634	12·952
12·5	1·6602	12·938
12·5	1·6624	12·955
12·5	1·6618	12·950
13·2	1·6581	12·928
13·2	1·6653	12·983
13·8	1·6598	12·945
14·4	1·6578	12·933
Average 12·6	1·6613	12·947

Chlorides of Olefines.

Methylene Chloride.

The first specimen of this product examined was prepared by the action of chlorine on methyl chloride (*Chem. Soc. J.*, **22**, 260). Distilled from phosphoric anhydride it mostly came over at 40°. The second specimen was from Kahlbaum ; this was also fractioned from phosphoric anhydride. The fraction boiling nearly constantly at 40° C. was used. The density determinations gave the following numbers :—

$$d\frac{15°}{15°} = 1·33771,$$

$$d\frac{25°}{25°} = 1·32197.$$

The density given by Thorpe (*Chem. Soc. J.*, **37**, 195) for this substance is considerably higher than the above, but from the boiling point he gives, and the method of preparation, there can be no doubt that the product was not quite free from chloroform.

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
11·0°	1·2171	4·276
11·0	1·2253	4·306
11·0	1·2224	4·296
11·0	1·2261	4·309
11·0	1·2276	4·314
11·0	1·2251	4·305
11·0	1·2321	4·329
11·8	1·2297	4·325
11·8	1·2206	4·292
11·8	1·2237	4·305
11·8	1·2187	4·287
14·0	1·2248	4·345
14·0	1·2255	4·348
14·0	1·2253	4·347
Average 11·9	1·2246	4·313

Ethylene Chloride.

This substance was distilled from phosphoric anhydride, and fractioned. The specimen examined boiled constantly at 83·7° corr. The density determinations gave—

$$d\frac{15°}{15°} = 1·25991,$$

$$d\frac{25°}{25°} = 1·24800.$$

Thorpe gives 83·5° as the boiling point; his density calculated for $d\frac{15°}{15°} = 1·25984$.

The following results were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
16·25°	1·2576	5·496
16·25	1·2576	5·496
16·25	1·2571	5·496
13·6	1·2568	5·476
13·6	1·2559	5·471
13·6	1·2562	5·473
Average 14·4	1·2569	5·485

Ethylidene Chloride—Methylmethylene Chloride.

This was from Kahlbaum and prepared from paraldehyde. It was distilled from phosphoric anhydride and fractioned. The speci-

men used boiled at 57—57·5°. The density determinations gave the following results:—

$$d\frac{15°}{15°} = 1·18450,$$

$$d\frac{25°}{25°} = 1·17120.$$

Thorpe's density, calculated for $d\frac{15°}{15°} = 1·18161$.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
16·5°	1·1509	5·352
16·5	1·1505	5·351
12·5	1·1505	5·318
13·0	1·1525	5·329
13·5	1·1513	5·327
Average 14·4	1·1511	5·335

Dimethylmethylene Chloride—Chloracetol.

This substance was prepared by the action of phosphoric chloride on pure acetone. It was repeatedly fractioned and boiled at 68·5—69·5° corr. Density determinations gave—

$$d\frac{15°}{15°} = 1·09620,$$

$$d\frac{25°}{25°} = 1·08430.$$

It was then distilled with phosphoric anhydride, when it boiled at 69·7—71·2° corr., and gave—

$$d\frac{15°}{15°} = 1·09657,$$

$$d\frac{25°}{25°} = 1·08476.$$

These numbers differ widely from those of Linnemann, which are given as 1·0827 at 16°.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
17·5°	1·1057	6·348
17·5	1·1066	6·354
17·5	1·1079	6·360
17·5	1·1072	6·357
16·0	1·1094	6·358
13·5	1·1037	6·308
14·6	1·1051	6·324
Average 16·3	1·1065	6·344

TRICHLORIDES.

Chloroform.

This substance was purified by fractional distillation from phosphoric anhydride. The specimen examined boiled constantly at 62° corr. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}50027,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}48432.$$

Thorpe's determination gives $d\frac{15^\circ}{15^\circ} = 1{\cdot}49966$.

It was refractioned from phosphoric anhydride and its density redetermined; it gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}50085,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}48492.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
13·5°	1·2647	5·587
14·0	1·2610	5·574
14·5	1·2552	5·551
15·0	1·2599	5·574
15·0	1·2601	5·575
16·8	1·2510	5 546
16·8	1·2468	5·540
16·8	1·2466	5·526
Average 15·3	1·2557	5·559

Methyl-chloroform.

This was obtained from Kahlbaum, and was purified by repeated fractional distillation from phosphoric anhydride. It then boiled at 75·3—76·3° corr., and the density determinations gave—

$$d\frac{15°}{15°} = 1{\cdot}32466.$$

$$d\frac{25°}{25°} = 1{\cdot}31144.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
14·0°	1·2000	6·712
14·0	1·2028	6·728
14·0	1·2028	6·728
20·8	1·2007	6·762
21·2	1·1970	6·743
21·6	1·2007	6·767
Average 17·6	1·2007	6·740

Vinyl Trichloride—Monochlorethylene Chloride.

This substance was purified in the same way as the preceding body. It boiled at 114·8—115·3°, and the density determinations gave—

$$d\frac{15°}{15°} = 1{\cdot}45527,$$

$$d\frac{25°}{25°} = 1{\cdot}44303.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
13·0°	1·3326	6·779
13·0	1·3390	6·796
14·0	1·3346	6·795
19·5	1·3307	6·807
20·0	1·3296	6·804
20·5	1·3261	6·789
Average 16·7	1·3321	6·796

Allyl Trichloride—Trichlorhydrin—Chlorotrimethylene Chloride.

This substance was made by passing chlorine into allyl iodide until the iodine liberated was converted into its chloride. The product was then washed with water, and the oil separated and washed with a little alkali. It was then dried over anhydrous potassium carbonate, and fractioned: the specimen examined boiled at 156—157°. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}39805,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}38753.$$

It was dried with phosphoric anhydride, refractioned, and then boiled at 157—158° corr. The density was—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}39836,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}38783.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
25·5°	1·3345	7·882
25·5	1·3365	7·895
25·5	1·3375	7·899
15·5	1·3485	7·905
16·0	1·3478	7·904
Average 21·6	1·3410	7·897

Carbon Tetrachloride.

This was purified by repeated fractional distillation with phosphoric anhydride. It boiled at 76·9° corr., and its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}60500,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}58873.$$

Thorpe's determination gives—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}60397.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
26·5	1·2198	6·585
27·5	1·2067	6·520
23·5	1·2271	6·609
23·5	1·2288	6·618
24·5	1·2205	6·578
Average 25·1	1·2206	6·582

Tribromides.

Bromoform.

As it was found that distillation appeared to cause decomposition to some extent, this substance was purified during the winter time by cooling it, thus causing it to crystallise. The crystalline mass was then broken up and pressed between porous plates, and again broken up and exposed to the air for an hour or two. It then had the appearance of small flakes of naphthalene and was quite white. The crystals melted at 7·8°. It was then melted, treated with phosphoric anhydride, filtered and distilled under reduced pressure (330 mm.), when it boiled at 120·3° corr., but became slightly yellow in colour. Density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 2{\cdot}90246,$$

$$d\frac{25^\circ}{25^\circ} = 2{\cdot}88253.$$

As slight decomposition had apparently taken place, it was slowly cooled, until about two-thirds had crystallised ; the crystals were then drained, and afterwards melted. The density determinations then gave—

$$d\frac{15^\circ}{15^\circ} = 2{\cdot}90450,$$

$$d\frac{25^\circ}{25^\circ} = 2{\cdot}88421.$$

So that even under the reduced pressure employed some decomposition had evidently occurred. That it becomes considerably

changed by distillation is evident from the result obtained by Thorpe (*Chem. Soc. J.*, **37**, 141), who purified his product by distillation alone. His density determinations give—

$$d\frac{15^\circ}{15^\circ} = 2{\cdot}79683,$$

$$d\frac{25^\circ}{25^\circ} = 2{\cdot}78275.$$

The fusing point of his product was only 2·5°.

The following numbers were obtained for the magnetic rotation of bromoform :—

t.	Sp. rotation.	Mol. rotation.
15·6°	2·3980	11·616
15·6	2·3998	11·626
16·5	2·4023	11·644
18·4	2·3935	11·616
18·9	2·3980	11·642
19·5	2·3918	11·617
20·5	2·3911	11·611
Average 17·9	2·3964	11·626

Vinyl Tribromide—Bromethylene Bromide.

This substance was prepared by acting on vinyl bromide with bromine. It boiled at 188·5—189·5° corr.

The density given by Anschütz (*Annalen*, **221**, 183) was used in the calculation:—

$$d\frac{17{\cdot}5^\circ}{17{\cdot}5^\circ} = 2{\cdot}62027,$$

$$d\frac{21{\cdot}5^\circ}{21{\cdot}5^\circ} = 2{\cdot}61418.$$

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
12·0°	2·2902	12·924
12·0	2·2844	12·891
12·0	2·2799	12·860
11·4	2·2878	12·906
11·4	2·2862	12·897
11·4	2·2886	12·910
11·4	2·2854	12·893
Average 11·7	2·2861	12·897

Allyl Tribromide—Tribromhydrin—Bromotrimethylene Bromide.

This was obtained from Kahlbaum. It was purified during the winter time by pressing the crystallised product between bibulous paper. The crystals were then melted, treated with a little phosphoric anhydride, and filtered. Thus obtained, its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 2{\cdot}41344,$$

$$d\frac{25^\circ}{25^\circ} = 2{\cdot}39856.$$

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	13·0°	2·1837	14·108
	13·0	2·1768	14·064
	13·0	2·1778	14·070
	22·75	2·1618	14·050
	23·25	2·1603	14·046
Average	17·0	2·1721	14·068

Bromethylene Dichloride—Vinyl Bromide Dichloride.

This body was prepared by gradually adding vinyl bromide to chloroform through which a current of chlorine was passing. When purified it boiled at 139—140° corr. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}86850,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}85420.$$

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	21·6°	2·0572	10·101
	21·6	2·0562	10·995
	21·6	2·0548	10·988
Average	21·6	2·0561	10·995

Unsaturated Compounds.

Allyl Alcohol.

This substance was obtained from Kahlbaum; it was dried with anhydrous copper sulphate, and also with caustic lime. It boiled at 96·8° corr. Its density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}85778,$$

$$d\frac{25°}{25°} = 0{\cdot}85067.$$

This is slightly heavier than the product examined by Thorpe, which gives $d\frac{15°}{15°} = 0{\cdot}85738$; but, although I treated it with the above dehydrating agents several times, I was unable to get the specimen any lighter.

The following numbers were obtained for the magnetic rotation of this body:—

t.	Sp. rotation.	Mol. rotation.
23·0°	1·2282	4·645
24·0	1·2275	4·646
13·0	1·2499	4·690
13·0	1·2496	4·688
13·0	1·2525	4·699
17·9	1·2463	4·693
17·9	1·2451	4·688
17·7	1·2448	4·686
21·5	1·2424	4·692
21·5	1·2430	4·695
Average 18·3	1·2229	4·682

Ethyl α-Crotonate, $CH_3.CH:CH.CO.OEt$.

The acid used for the preparation of this ether was obtained from Kahlbaum; it was the α-compound, $CH_3.CH:CH.COOH$, melting at 72°. It was etherified with alcohol and hydrochloric acid in the usual way. The ethereal salt boiled at 138—140° corr., and the density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}92680,$$

$$d\frac{25°}{25°} = 0{\cdot}91846.$$

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	22·5°	1·0998	7·567
	23·5	1·1034	7·601
	24·0	1·1030	7·599
	25·5	1·1052	7·624
	25·0	1·1009	7·591
	25·0	1·0980	7·571
	25·5	1·0970	7·568
Average	24·4	1·1010	7·589

Ethyl Oleate.

The acid employed in the preparation of this salt was from Kahlbaum. Oleic acid was found to etherify very readily when treated with alcohol and hydrochloric acid gas. The product was washed with water (it cannot be washed with a solution of alkaline carbonate, as it generally forms an emulsion), mixed with ether, and dried over anhydrous potassium carbonate. After distilling off the ether on the water-bath, the ethyl oleate was fractioned several times under reduced pressure. The specimen taken boiled at 306—308° under 307 mm. (half the mercury column only in vapour). The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}87589,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}87041.$$

When refractioned under the same pressure and with the thermometer in the same position, this gave, as the principal fraction, a product boiling at 304·75—307·25°. The density determinations of this gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}87525,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}86991.$$

This slight difference in density indicates that the product was as pure as could be expected for such a body.

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	13·8°	1·1162	21·950
	13·7	1·1135	21·886
	14·4	1·1149	21·931
	14·6	1·1137	21·910
	17·8	1·1103	21·888
	17·8	1·1103	21·888
Average	15·0	1·1148	21·909

Ethyl Allylmalonate.

This substance was made by Conrad's process. It boiled chiefly at 222—223° corr. It was then saponified, the acid thrown down in the usual way as calcium salt, separated with hydrochloric acid, and taken up with ether. After separating the ether, the acid was crystallised and then etherified.

Ethyl allylmalonate prepared in this way boiled at 193·5—194·5° (column in vapour) under 330 mm. The density determinations gave—

$$d\frac{15°}{15°} = 1·01397,$$

$$d\frac{25°}{25°} = 1·00620.$$

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	14·1°	1·0298	11·277
	14·1	1·0284	11·261
	14·1	1·0281	11·258
	13·0	1·0342	11·315
	13·6	1·0310	11·285
	13·6	1·0313	11·289
Average	13·7	1·0305	11·281

Ethyl Diallylmalonate.

This substance was prepared in the way described by Conrad, and fractioned under reduced pressure; it boiled at 201—204° (column in vapour) under 225 mm. The density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}99997,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}99301.$$

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	22·0°	1·1237	15·052
	22·0	1·1170	14·966
	22·0	1·1178	14·977
Average	22·0	1·1195	14·998

As the product used in these observations had not been purified in the same manner as most of the other malonic derivatives, endeavours were made to render it purer. It was therefore saponified with alcoholic potash, the alcohol evaporated, and the saline mass dissolved in a little water and neutralised with hydrochloric acid; calcium chloride was then added, which caused calcium diallylmalonate to precipitate, and after standing about 24 hours, this was collected and well pressed. Conrad states that diallyl malonate is not precipitated under these conditions; it was found, however, that it is simply a matter of the concentration of the saline solution and of the calcium chloride used, and unless they are strong no precipitation takes place. The calcium diallylmalonate, when treated with strong hydrochloric acid, formed a crystalline magma of the acid. This was taken up with ether, and the ethereal solution evaporated.

The resulting acid was dissolved in hot water and allowed to stand, it then crystallised out most beautifully, in long thick prisms; these, when recrystallised, fused at 134°. It is only moderately soluble in cold water. This acid forms a beautiful crystalline, but difficultly soluble barium salt, as described by Conrad.

The acid was then dissolved in alcohol, the solution saturated with hydrochloric acid, and allowed to stand for 24 hours; the excess of alcohol was distilled off, water added, and the oil taken up with ether. On washing the ethereal solution with sodium carbonate, however, nearly all the product it contained dissolved, and was reprecipitated by acid. As it was apparently the acid ethereal salt, it was separated and re-treated with alcohol and hydrochloric acid, but the result was the same, very little product insoluble in sodium carbonate being formed. I have not further examined into this anomalous result, nor yet

obtained sufficient ethyl diallylmalonate by this process, for further examination.

Ethyl Allylacetoacetate.

This substance was prepared in the usual way from ethyl acetoacetate, and boiled at 213—214° corr. at 720 mm. Its density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}99272,$$

$$d\frac{25°}{25°} = 0{\cdot}98542.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
11·0°	1·0942	10·379
11·0	1·0954	10·391
13·2	1·0930	10·384
15·3	1·0918	10·391
15·5	1·0918	10·391
15·5	1·0922	10·395
15·8	1·0867	10·345
Average 13·9	1·0922	10·382

UNSATURATED HALOGEN COMPOUNDS.

Bromethylene—Vinyl Bromide.

This substance was obtained in the usual way by acting on ethylene bromide with alcoholic potash. It was washed, dried, and finally distilled from phosphoric anhydride. It boiled at 16° corr. The following density determination was made with a freshly distilled product; this is a necessary precaution as this body quickly polymerises on keeping.

$$d\frac{9{\cdot}6°}{9{\cdot}6°} = 1{\cdot}52504.$$

Other determinations had been previously made in an ordinary Sprengel tube, the results were a little lower, most likely owing to loss from evaporation. I have, however, used the change of density they gave, viz., 0·00227 for 1°, in the following calculation, but although probably not far wrong, it yet requires to be redetermined.

The following numbers were obtained for its magnetic rotation, a freshly distilled product being used:—

t.	Sp. rotation.	Mol. rotation.
5·5°	1·6109	6·241
5·5	1·6112	6·242
5·5	1·6114	6·243
8·5	1·5892	6·188
11·0	1·5894	6·208
11·0	1·5868	6·198
Average 7·8	1·5998	6·220

Chloropropylene—Allyl Chloride.

$CH_2 : CH.CH_2Cl$.

To prepare this body, allyl alcohol was heated with phosphorus trichloride; on distilling this mixture on the water-bath the chloride soon commences to come over. The product in the retort, however, becomes opaque and of an orange colour, and a quantity of fine powder, like amorphous phosphorus, forms, and gradually increases, and in the course of about half an hour there is a rush of gas, apparently phosphoretted hydrogen, which explodes, and in one instance the apparatus was destroyed. This behaviour is quite different to that which takes place when other chlorides are made with phosphorous trichloride, though in the latter cases, when high temperatures are employed, phosphoretted hydrogen is given off, probably from the decomposition of phosphorous acid. The allyl chloride was washed, dried, and distilled from phosphoric anhydride; it boiled at 45—46° corr., and its density determinations gave—

$$d\frac{15°}{15°} = 0{\cdot}94366,$$

$$d\frac{25°}{25°} = 0{\cdot}93228.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
26·0°	1·3181	6·017
26·0	1·3111	5·986
26·0	1·3168	6·010
17·6	1·3359	6·036
18·4	1·3362	6·043
14·3	1·3319	5·994
14·3	1·3319	5·994
14·3	1·3303	5·987
Average 19·6	1·3265	6·008

Bromopropylenes—I. *Methylvinyl Bromide.*

$CH_3.CH : CHBr$.

This substance was prepared by Reboul's process (*Ann. Chim. Phys.* [5], **14**, 477), which consists in treating the mixture of bromopropylenes, obtained by acting on propylene bromide, $CH_3.CHBr.CH_2Br$, with alcoholic potash, with concentrated hydrobromic acid for about a week. The bromopropylene $CH_3.CBr : CH_2$ combines with the acid, the isomer $CH_3.CH : CHBr$ remaining mostly unacted upon, so that a mixture consisting of this latter body, $CH_3.CBr_2.CH_3$ and propylene bromide is obtained, and on account of the difference in the boiling points the bromopropylene can easily be separated.* $CH_3.CH : CHBr$ thus prepared, boiled between 59° and 63° corr. Reboul gives it as 59·5—60°; unfortunately the quantity obtained was too small to allow of its further purification by fractional distillation. The density determinations gave—

$$d\frac{15°}{15°} = 1{\cdot}42077,$$

$$d\frac{25°}{25°} = 1{\cdot}40527.$$

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
27·5°	1·5254	7·318
27·5	1·5217	7·299
26·5	1·5221	7·293
22·0	1·5290	7·289
22·0	1·5286	7·289
22·0	1·5253	7·272
22·0	1·5325	7·307
Average 24·2	1·5264	7·295

II. *Allyl Bromide.*

$CH_2 : CH.CH_2Br$.

This was obtained from Kahlbaum, and was purified by fractional distillation from phosphoric anhydride. It boiled at 70—71° corr., and its density determinations gave—

* The higher fractions were employed for the preparation of the bromide, $CH_3.CBr_2.CH_3$ (see p. 524).

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}42532,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}41057.$$

The following numbers were obtained for its magnetic rotation :—

	t.	Sp. rotation.	Mol. rotation.
	17·0°	1·7413	8·230
	17·5	1·7401	8·228
	18·2	1·7421	8·247
	18·3	1·7439	8·255
	19·0	1·7367	8 225
	19·0	1·7378	8·230
	18·0	1·7321	8·194
	13·8	1·7406	8·199
	13·8	1·7409	8·201
	13·8	1·7417	8·206
Average	16·8	1·7398	8·221

Iodopropylene—Allyl Iodide.

$CH_2{:}CH.CH_2I$.

This iodide was purified by agitation with mercury until free iodine was removed; it was then immediately filtered off, dried with phosphoric anhydride, and fractioned under reduced pressure. It was thus obtained as a very pale straw-coloured liquid, boiling at 70—71·5° corr. under 330 mm. Its density determinations gave—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}82403,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}80776.$$

The following numbers were obtained for its magnetic rotation, the product used being freshly distilled :—

	t.	Sp. rotation.	Mol. rotation.
	19·5°	2·4901	12·793
	20·0	2·4874	12·785
	20·5	2·4859	12·783
	17·5	2·4956	12·799
	18·0	2·4933	12·792
	18·5	2·4894	12·778
Average	19·0	2·4903	12·788

Observations on the Relative Densities and Specific Magnetic Rotations of the Bodies Examined.

Before considering the numbers representing the molecular rotation of the substances examined, it will be of some interest to consider the relationship of the various densities and specific rotations to each other, comparing them at a definite temperature.

The series of bodies which are the most extensive and lend themselves best to this are those of the fatty acids and their ethereal salts (ethers). In the accompanying diagram (Diag. III) the results previously given in this paper, recalculated for 20° C., have been plotted out. The abscissæ represent the number of carbon-atoms contained in the substances, the ordinates being a scale of numbers indicating to the third place of decimals, and including those of the densities and specific rotations.

It will be seen that the densities of both acids and ethereal salts form regular curves, the curve of the latter being more contracted than that of the former, as described to the Society on a previous occasion.

Having observed the relationship of the ethylic salts of the fatty acids, it appeared to be of interest to see what kind of curve would be formed by a series in which the acid radicals remained the same and the alcohol radical varied; a comparison was therefore made between—

Acetate of methyl,
„ ethyl,
„ propyl,
„ octyl,
„ cetyl.

These do not form precisely the same curve as the ethylic salts, but one that crosses it and which is slightly more contracted.

A third comparison was also made in which both acid and alcohol radicals vary equally. The following were taken :—

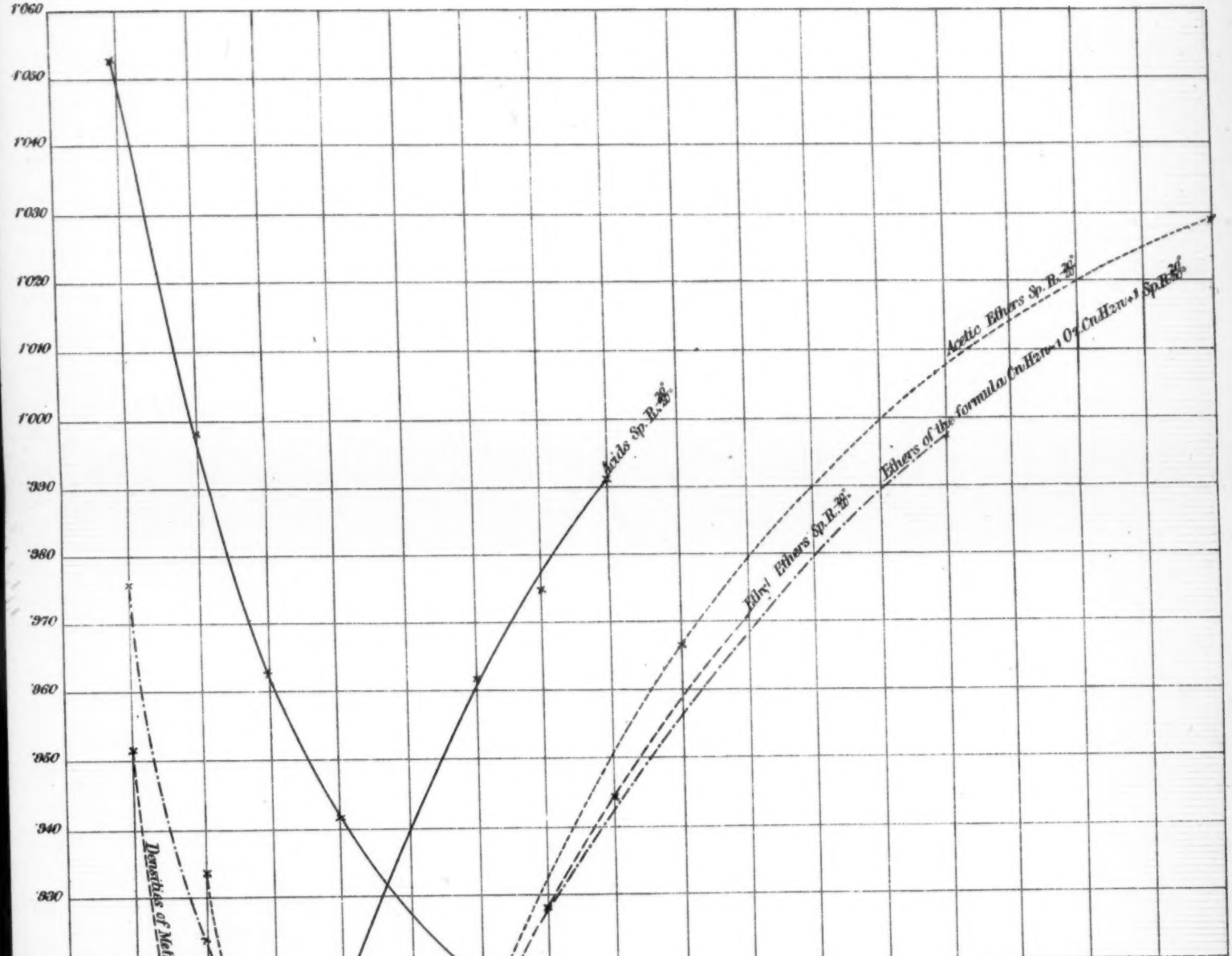
Formate of methyl,
Acetate of ethyl,
Propionate of propyl,
Œnanthate of heptyl.

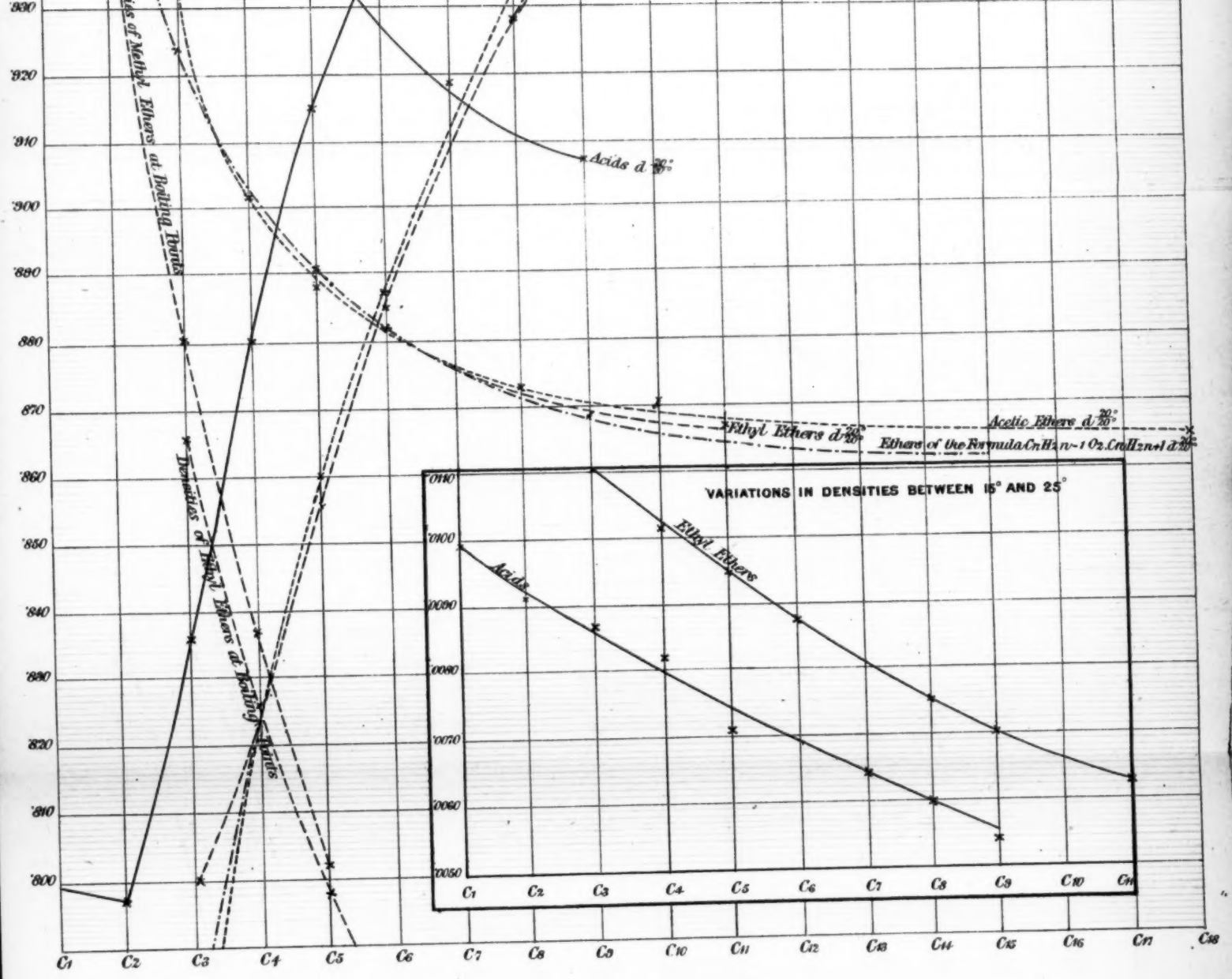
In this case a curve is formed slightly more open than in the case of the ethylic salts, but following it for a considerable distance.

Whilst engaged in determining the densities of bodies of the homologous series, it was noticed that the rates of expansion became less with increase of molecular weight: this diminution taking place in a regular manner. This will be seen from the small diagram on Diag. III, which shows the change of density of the fatty acids and their

DIAGRAM 3.

CURVES FORMED BY DENSITIES AND SPECIFIC ROTATIONS OF $C_nH_{2n}O_2$ ACIDS AND THEIR ETHERS (ETHEREAL SALTS).





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ethylic salts between 15° and 25°; and from this it will be observed that they follow two curves pretty closely, the greatest deviation being only 0·0003. This matter was also brought under the observation of the Society some time since.

It would appear from the foregoing that the densities of homologous bodies follow each other in a definite manner, and thus obey a distinct law. The same appears to be true of the rates of expansion. These observations make it important that such determinations should be made as carefully as possible, especially as they may prove of value in determining the constitution of bodies.

With the present density determinations no regular curve can be obtained with the normal primary alcohols, but this is probably due to a want of purity in the products examined, as many of them are difficult to obtain in quantity. But commencing with ethyl alcohol, and taking with it propyl, butyl (Linnemann's determination) and octyl alcohols, a curve can be formed to include them. Heptyl alcohol is also not far away from it; there can, however, be but little doubt that this alcohol, prepared from œnanthaldehyde, contains some impurity, because its density is slightly higher than that of octyl alcohol, whereas in the alcohols the density always increases with the molecular weight.

The comparison of densities at a given temperature is sometimes thought to be of but little value. In a series of homologous bodies, however, they are comparable, because between each member of the series there is the same difference of composition, practically the same difference in boiling point, and a regular difference in the rate of expansion, and the result of calculating the numbers out to the boiling point of the substance would only be to make the curve approach a straight line. On the diagram a few ethereal salts (ethers) are plotted out at their boiling point, the densities taken at those temperatures being those given by Elsässer (*Annalen*, **218**, 302).

These remarks also apply to the specific rotation which, by reference to the diagram, will also be seen to form curves but of course in the opposite direction to the densities. Formic acid, however, it will be seen, does not form part of the curve, and in the case of the ethereal salts it will also be noticed that a slight change of direction takes place between ethyl formate and ethyl acetate. The regularity of these curves indicates that the numbers obtained by the observations of the magnetic rotation, from which they are deduced, are very near the truth, or at any rate quite consistent.

Molecular Rotation. Normal Compounds.

In the short paper I brought before the Society in reference to this subject in 1882, I stated, from the data I then had, that the

molecular magnetic rotation of a body evidently varies with the chemical composition in a regular or comparatively regular manner, and that for every addition of CH_2 there is an increase of from 1·0 to 1·2. As the series of fatty acids and of their ethereal salts are the most extensive which have been examined, it will perhaps be best to commence by referring to them.

When considering the numbers obtained on the further examination of these series, I was led to think that this number was exactly 1·0, and that the small differences observed were due to errors of observation. On measuring œnanthylic acid and its ethyl salt, however, numbers were obtained which were inconsistent with this assumption. As these substances were difficult to measure, owing to small changes of temperature causing convection, it was thought that this apparent inconsistency might be due to errors caused by this difficulty, or from some impurity in the product. The substances were therefore repurified and fractioned. As this did not cause any change, some other higher acids and ethereal salts were measured, and the result of their examination was the discovery of the fact that the value of the difference of CH_2 was greater than 1·0. From a very large number of observations it has been found to be as nearly as possible 1·023.

Having obtained this result, it is found possible to calculate the molecular rotation of any member of a homologous series if but one member be well examined, all that is necessary being to add or subtract this number as many times as the difference of composition may require; or a simple formula may be used. Taking œnanthylic acid as an example, if we take its molecular rotation and subtract from it $1·023 \times 7$ we get a residue in excess of that which the product would give if it consisted of CH_2 only, thus:—

Mol. rotation of œnanthylic acid..	7·552
$1·023 \times 7$	7·161
	0·391

This residual number it is proposed to call the *series constant*, and designate by *s*. From this we may construct a formula for the normal acids of this series (commencing with propionic acid)—

$$C_nH_{2n}O_2 = 0·391 + n(1·023).$$

The series constant is very useful in comparing the different series of bodies in relation to each other.

The following is a comparison of the molecular rotation found for the acids of the fatty series and those calculated:—

	Found.	Calculated.
Propionic acid	3·462	3·462
Butyric acid	4·472	4·485
Isobutyric or Dimethacetic acid.....	4·479	4·485
Valeric acid	5·513	5·508
Œnanthylic acid	7·552	7·554
Caprylic acid.....	8·565	8·577
Nonylic acid	9·590	9·600

For the ethereal salts, the series constant is taken as 0·337; the following are the results compared with the calculated values :—

	Found.	Calculated.
Ethyl propionate	5·452	5·452
Ethyl butyrate	6·477	6·475
Ethyl dimethacetate.....	6·479	6·475
Ethyl caproate	8·509	8·521
Ethyl œnanthate	9·541	9·544
Ethyl nonate.....	11·571	11·590
Heptyl œnanthate	14·655	14·659

It will be seen that the numbers found agree very closely for the difference of $CH_2 = 1·023$.

Formic and acetic acids and their ethereal salts, judging from their molecular rotations, evidently do not belong to the homologous series. This matter will be referred to further on.

For the ethereal salts of acetic acid the series constant is 0·370, and the following is a comparison of the values calculated and found :—

	Found.	Calculated.
Ethyl acetate	4·462	4·462
Propyl „	5·487	5·485
Octyl „	10·601	10·600
Cetyl „	18·772	18·784

To make the results obtained more intelligible, they have been represented graphically, and will be seen on the diagrams at the end of this paper. In these the abscissæ refer to the number of carbon-atoms contained in the substances, and the ordinates are the decimal numbers of the molecular rotation. The whole numbers have been disregarded, because by so doing the figures can be indicated to the third decimal place, which is important, and to do this and introduce the whole numbers would require diagrams ten times as large as the accompanying ones, which furnish all the information of special interest. To save reference to the body of the paper it is to be observed that when it is wished to know the molecular rotation of any

substance containing carbon, hydrogen, and oxygen, and referred to in the diagram, it is only necessary to add together the numbers of the abscissæ and ordinates which correspond to it. When the rotations are higher, as in the halogen compounds, the numbers may be found in the same way, but adding to it the numbers given in connection with the diagram.

From Diagram VI, referring to the acids and ethereal salts, it will be seen how the molecular rotation drops from formic to acetic acid, and again, but in a less degree, to propionic acid, the line then becoming an ascending straight line. This is also seen with the ethereal salts which run nearly parallel with the acids; the drop is, however, about a fourth less in the first two members of these series than in the case of the acids. It will also be observed that the acetates form a distinct line for themselves, differing from the salts of the homologous series in the same way, though not to the same extent, as acetic acid does from its homologues.

Having found the value of the difference for $C\dot{H}_2$ between members of the series of fatty acids and their ethereal salts to be a constant quantity, and the molecular rotation—as will be observed by reference to the numbers—the same for normal salts having the same composition and containing ethyl or higher radicals, it is of interest to see whether the number holds good in other series. For this purpose the paraffin series may be selected.

In this series heptane, from *Pinus sabiniana*, was the most carefully examined, as it was the most reliable body in respect to purity: the series constant deduced from the examination of this body is 0·513.

The following is a comparison of the numbers calculated and found. (See Diagram V):—

	Found.	Calculated.
Pentane.....	5·638	5·623
Hexane	6·670	6·646
Heptane.....	7·669	7·669

These results are quite as close as could be expected considering the difficulty of obtaining pentane and hexane pure, and they may fairly be assumed to follow the same law as the acids and ethereal salts already considered.

The same thing is found to hold good in the series of normal alcohols commencing with propyl alcohol. In this case the series constant is 0·699. The following results have been obtained. (See Diagram IV):—

	Found.	Calculated.
Propyl alcohol	3·768	3·768
Heptyl „	7·850	7·860
Octyl „	8·880	8·883

DIAGRAM 4.

$C_nH_{2n+2}O$ ALCOHOLS & ETHERS (OXIDES).

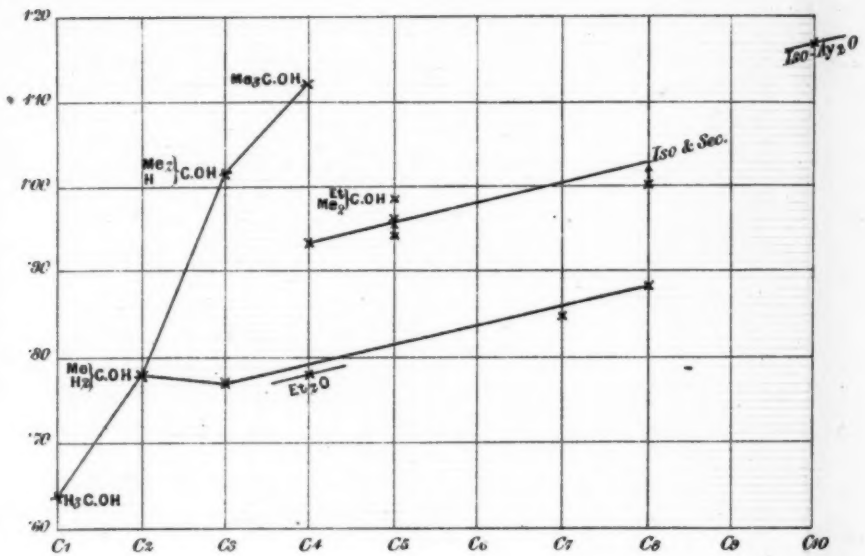


DIAGRAM 5.

PARAFFINS, ALDEHYDES AND KETONES.

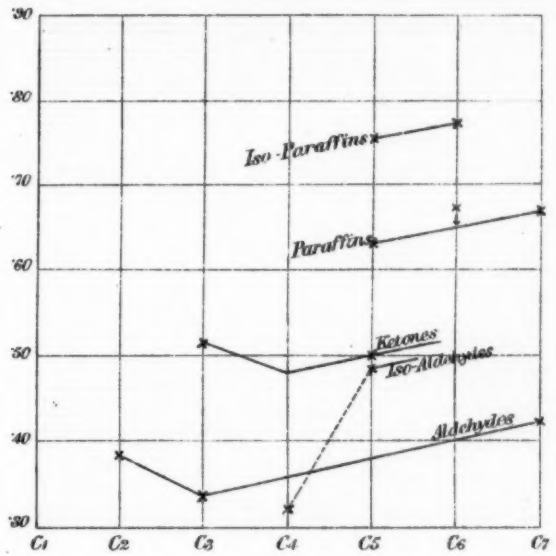
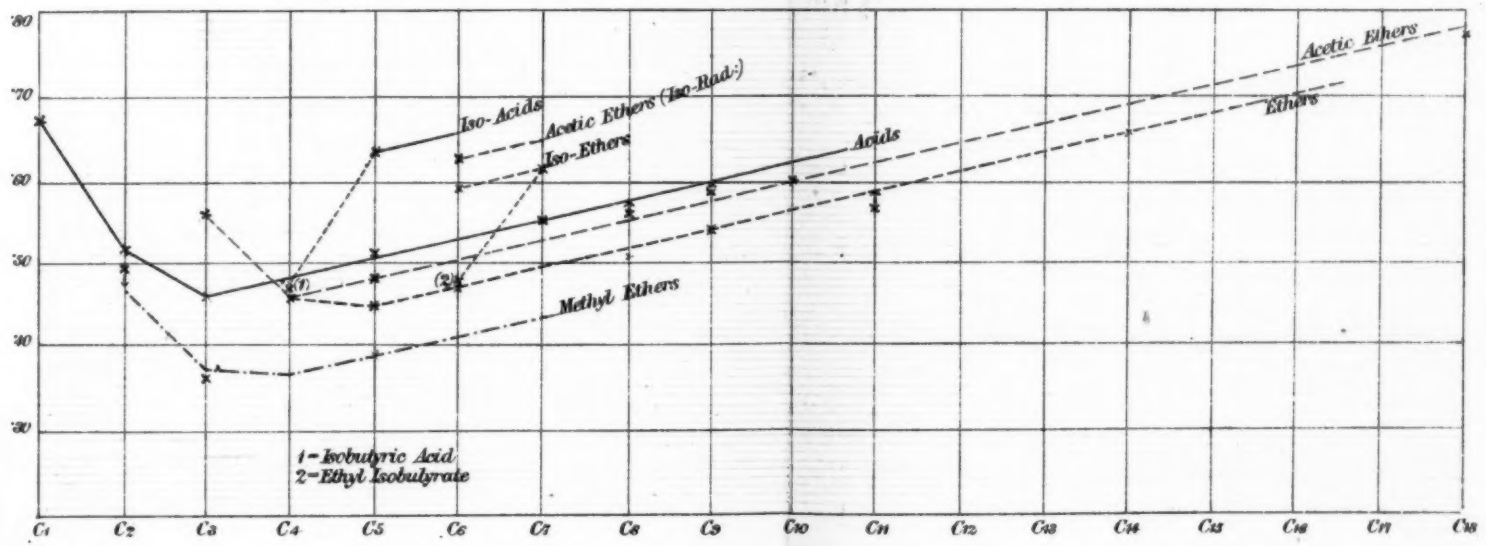


DIAGRAM 6.

$C_nH_{2n}O_2$ ACIDS AND THEIR ETHERS (ETHEREAL SALTS).



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The aldehydes commencing with propyl aldehyde also appear to follow the same law. (See Diagram V.) The series constant is 0·263 :—

	Found.	Calculated.
Propyl aldehyde	3·332	3·332
Œnanthaldehyde	7·422	7·424

In the succinic series we get the following numbers. (See Diagram X.) The series constant is 0·196 :—

	Found.	Calculated.
Ethyl succinate.....	8·380	8·380
„ suberate	12·461	12·472
„ sebate	14·496	14·518

The monobasic unsaturated acids in the series appear also to follow the same law. Two only have been examined, but as they are far apart the results are important as confirming the value of CH_2. The series constant is 1·451.

	Found.	Calculated.
Ethyl crotonate	7·589	7·589
„ oleate	21·909	21·897

The chlorides, bromides and iodides of the normal alcohol radicals also appear to give similar results, commencing with the propyl compounds. The series constants are—

Chlorides	$s = 1·988$
Bromides	3·816
Iodides	8·011

As the higher members of these series are difficult to get pure, the numbers are not quite so close as in the other cases.

	Found.	Calculated.
Propyl chloride.....	5·056	5·056
Octyl „	10·128	10·173
Propyl bromide.....	6·885	6·885
Octyl „	12·025	12·000
Propyl iodide.....	11·080	11·080
Octyl „	16·197	16·196

Influence of the Displacement of Hydrogen by Methyl in Normal Homologous Compounds.

The bodies formed in this manner which it is proposed to consider first, are the iso- and secondary bodies.

Isoparaffins.

These may be considered as normal paraffins in which an atom of hydrogen has been displaced by methyl in the CH_2-group already associated with methyl, thus:—

$CH_3.CH_2.CH_2.CH_3$	$(CH_3)_2CH.CH_2.CH_3$.
Butane.	Methylbutane or isopentane.
$CH_3.CH_2.CH_2.CH_2.CH_3$	$(CH_3)_2CH.CH_2.CH_2.CH_3$.
Pentane.	Methylpentane or isohexane.

The influence of the introduction of methyl on the molecular rotation is very marked, as it increases the rotation to a considerably greater extent than would result from the change in composition caused by the introduction of CH_2, as the following comparisons show. The series constant for the isoparaffins is 0·631 (see Diagram V):—

		Diff. for CH_2.	
Isopentane	5·750	0·112	1·019
Pentane	5·638		
Isohexane	6·769	0·099	
Hexane	6·670		

It will be observed, however, that the difference found for the increase of CH_2 between the two iso-compounds themselves is practically the same as that in other series.

Iso-alcohols.

The following are the differences between the normal and iso-alcohols (see Diagram IV).

		Diff. for CH_2.	
Isobutyl alcohol.....	4·936	0·14	1·023
Normal butyl alcohol (calc.)...	4·791		
Isoamyl alcohol* (inactive)....	5·959	0·145	
Normal amyl alcohol (calc.) ..	5·814		

The series constant for these is 0·844. The increase of rotation is slightly higher than in the case of the iso-paraffins. Here again the difference between the two iso-alcohols is practically the same as in other series for the difference CH_2.

Isoamyl oxide which contains two isoamyl groups shows, as might be expected, about double the difference noticed for the alcohol. The series constant is 0·932.

* The active isoamyl alcohol examined gave, as already noticed, somewhat lower numbers than the inactive. From its permanent rotation it evidently consisted chiefly of the inactive, so that it is possible that the pure active alcohol would give a considerably lower rotation, which is to be expected if it contain an ethyl group.

Isoamyl oxide.....	11·168	0·288 = 0·144 × 2.
Normal amyl oxide (calc.) ..	10·880	

The calculated number for normal amyl oxide is based on the assumption that its series constant differs from normal amyl alcohol in the same way as ethyl oxide differs from ethyl alcohol (see Diagram IV).

Iso-acids and Ethereal Salts.

In the case of the iso-acids and their ethereal salts, the products which have been examined are—

Isovaleric acid	5·635	0·122
Normal valeric acid	5·513	
Ethyl isovalerate	7·615	0·117
„ normal valerate (calc.)	7·498	
„ isopropyl malonate.....	10·482	0·115
„ normal propyl malonate....	10·367	

In the two following cases we have examples where one or two iso-radicals replace hydrogen in hydroxyl :—

Isobutyl acetate.....	6·623	0·115
Normal butyl acetate (calc.)	6·508	
Isobutyl succinate.....	12 707	0·235 = 0·117 × 2
Normal butyl succinate (calc.) ..	12·472	

Diagrams VI and X.

Aldehydes:

In the case of the aldehydes, one example only can be given :—

Isovaleric aldehyde.....	5·487	0·111
Normal valeric aldehyde (calc.)	5·376	

Diagram V.

The results show that the increase of the molecular rotation caused by the introduction of methyl so as to form *iso*-compounds, is beyond that which would ordinarily result from the introduction of CH_2 by the following amounts :—

	Mean.	
Iso-alcohols	0·144	
„ oxides	0·144	
„ acids.....	0·113	mean = 0·112.
Ethereal salts containing iso-radicals	0·117	
Iso-aldehydes	0·111	
Iso-paraffins	0·105	

In the case of the iso-alcohols and oxides, it is evidently slightly

higher than in the other instances, but the difference in the last four examples is probably due to errors of observation, &c., and the mean is most likely applicable to all.

The consideration of one iso-acid, its ethereal salt and aldehyde has been omitted, viz., isobutyric acid, ethyl isobutyrate, and isobutyric aldehyde. These have given the following numbers, which it will be seen are nearly identical with those of normal bodies (see Diagrams V and VI).

Isobutyric acid	4·479
Normal butyric acid.....	4·472
Ethyl isobutyrate	6·479
Normal ethyl butyrate.....	6·477
Isobutyric aldehyde	4·321
Normal butyric aldehyde (calc.).....	4·353

There are several points to be considered in connection with these substances, such as the influence of CO.OH on groups connected to it, and on the subject of where homologous series truly begin. The former subject it is intended to refer to further on, but the latter may be considered here. From the numbers which have been obtained, and from a consideration of the subject, it appears that any body to be the first member of a homologous series must contain the CH_2-group, because it is by the introduction of additional members of this group that we form these series. Thus propionic acid should be the first member of the homologous series of acids. Formic and acetic acids do not contain the CH_2-group, and they are well known to possess properties which are not altogether comparable with those of the other fatty acids. The magnetic rotation of these bodies, as referred to above, indicates the same thing.

Now with reference to the isobutyric series, we have to deal with bodies which do not contain CH_2, and do not give rotations comparable with those of iso-compounds; but the moment we introduce into them this group, they immediately behave as other iso-derivatives, their rotation rising. Of course this addition converts isobutyric into isovaleric compounds, which have already been considered. The dotted lines joining these in Diagrams IV, V, and VI, are intended to draw attention to this fact. This remarkable change in the rotation is also thought to be to some extent due to the separation of the iso-group from the influence of the COOH and COH-groups by the introduction of the CH_2-group.

Influence of the Displacement of Hydrogen in Normal Bodies so as to form Secondary Compounds.

This displacement is, in this case, in the carbon-group associated with hydroxyl or other negative radical, thus :—

$CH_3.(CH_2)_5.CH_2.OH$	$CH_3.(CH_2)_5.C(CH_3)H.OH.$
Heptyl alcohol.	Methyl heptyl alcohol.
	Sec. octyl alcohol.

The secondary octyl alcohol is the only true instance of this kind of displacement I have examined which contains only carbon, hydrogen, and oxygen. Halogen-derivatives have, however, been studied, and are referred to further on. This alcohol gave the following number for its molecular rotation :—

Secondary octyl alcohol	9·004	0·124.
Normal octyl alcohol	8·880	

This difference varies only from that found for iso-alcohols by 0·023, an amount which may be quite accounted for by errors of observation, &c., though secondary bodies are believed to give slightly higher results.

Isopropyl alcohol is also a secondary compound, but is not a member of the homologous series according to the considerations above given. The rotation is remarkably high. The following is the comparison with the normal alcohol :—

Isopropyl alcohol	4·019	0·251
Normal propyl alcohol	3·768	

The isopropyl radical, however, except in the case of isobutyric compounds referred to, and in that of the alcohol, behaves much in the same way as a secondary compound.

The halogen derivatives will be referred to further on.

So far then as experiments have been made, the introduction of methyl so as to convert primary into secondary bodies, has practically the same influence on the molecular rotation as when it takes place in such a manner as to form iso-derivatives. (See Diagrams IV and VI.)

Displacement of Hydrogen in Aldehydes by Methyl so as to form Ketones.

Acetone and methyl propyl ketone are two cases which have been examined in relation to this point. As acetic aldehyde with which acetone has to be compared has no homologue, it is necessary to add

1·023 to the rotation of this substance to make up for the addition of CH_2 which has occurred in converting it into acetone:—

Acetone	3·514	0·106
Acetic aldehyde + 1·023 = ...	3·408	
Methyl propyl ketone	5·499	0·123
Valeraldehyde (calc.)	5·376	

It will be observed that methyl propyl ketone has practically the same rotation as isovaleraldehyde. In fact, it is seen that this displacement by methyl raises the molecular rotation in the same way as when converting normal aldehydes into iso-aldehydes. (See Diagram V.)

Displacement by Methyl and Ethyl of the Hydrogen in Methyl Alcohol.

The displacement referred to is that of hydrogen in the methyl-group, whereby, in the first instance, this alcohol is converted into ethyl alcohol. This raises the rotation:—

Ethyl alcohol	2·780	0·117
Methyl alcohol + 1·023	2·663	

The rotation of ethyl alcohol is proportionally higher than that of the homologous alcohols by about 0·035.

The introduction of a second methyl group results in the formation of secondary or isopropyl alcohol. Here we get an exceptionally large rise in the molecular rotation, as already referred to. The following is a comparison of it with ethyl alcohol:—

Isopropyl alcohol (dimethyl carbinol)	4·019	0·216
Ethyl alcohol + 1·023	3·803	

By the introduction of a third methyl group, as in the formation of tertiary butyl alcohol, a further rise is produced:—

Tertiary butyl alcohol (trimethyl carbinol)	5·122	0·080
Isopropyl alcohol + 1·023	5·042	

With reference to the displacement of hydrogen by ethyl, only one instance can be given: it is, however, somewhat remarkable. The body examined was dimethylethylcarbinol, which may be viewed as methyl alcohol with two atoms of hydrogen displaced by methyl and one by ethyl, or as ethylisopropyl alcohol. This body has a relatively lower rotation than isopropyl alcohol itself:—

Tertiary amyl alcohol (dimethyl ethyl carbinol)	5·987
Isopropyl alcohol + 1·023 × 2	6·065

The rotation is nearly identical with that of isoamyl alcohol, which is 5·959. There can be no doubt that isopropyl alcohol has an abnormally high rotation, and is therefore scarcely a good member to make comparison with, especially as dimethylcarbinyl acts in other combinations in a more normal manner. However, until more information has been obtained respecting the displacement of hydrogen in radicals by ethyl, little can be deduced from this case.

All these derivatives of methyl alcohol stand alone, and are only interesting when viewed in relation to each other, except that they show that the influence of the displacement of hydrogen by methyl is to raise the molecular rotation as is seen in other cases. (See Diagram IV.)

There is another case of displacement of hydrogen by methyl which may perhaps be referred to here, and that is in ethylene alcohol or glycol. The substance is pinacone or tetramethylglycol:—

$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}C.OH$$
$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}C.OH$$

In this case, the rise of molecular rotation over the usual amount for change of composition is very considerable; but not nearly four times the amount which arises from the displacement of one of methyl in ordinary alcohols. However, from the examination of the mono-, di-, and tri-methyl derivatives of ethylene bromide, it is found that the effect becomes smaller each time the displacement is effected, and that if plotted out the results form a curved line, so that it is quite likely that the first introduction of the methyl group into glycol will be found, when examined, to have as much, or nearly as much, effect as when it takes place in an ordinary alcohol. The following is the comparison with glycol:—

		Diff. for replacement by $CH_3 \times 4$.
Pinacone.....	7·245	0·210
Glycol 2·943 + 1·023 × 4	7·035	

See Diagram VII.

Displacement of the Hydrogen of Hydroxyl by Methyl, Ethyl and other Normal Radicals.

I. Ethyl Salts.

It will be most convenient to consider the ethyl before the methyl salts.

The effect of the conversion of an acid into its ethyl salt is to

reduce its magnetic rotation. It will be well to compare the ethereal salts of those acids which have no homologue first:—

Formic acid 1·671 + 1·023 × 2....	3·717	0·153
Ethyl formate	3·564	
Acetic acid 2·525 + 1·023 × 2	4·571	0·109
Ethyl acetate.....	4·462	

If we compare the acids and ethereal salts of the homologous acids, we get—

Propionic acid 3·462 + 1·023 × 2..	5·508	0·056
Ethyl propionate	5·452	

which is apparently a constant difference existing between the two series.

II. Other Ethereal Salts containing Normal Radicals.

Although ethyl is not believed to be strictly a member of the homologous series, yet its influence on the magnetic rotation is in most compounds practically the same as though it were,—ethylic alcohol being the chief exception, where it is about 0·035 higher than it should be if it were a member of the series. This is found to be the case in the series of the ethereal salts of the fatty acids, judging from propyl acetate as compared with ethyl acetate, so that all ethereal salts containing normal radicals appear to possess the same series constant, and therefore can be represented by the same formula,* methyl salts excepted. (See Diagram VI.)

III. Methyl Salts.

The displacement of the hydrogen of the hydroxyl of an acid by methyl produces a greater reduction of the magnetic rotation than does that by ethyl.

Thus, taking again the acids which have no homologues, we get—

Formic acid 1·671 + 1·023.....	2·694	0·199
Methyl formate	2·495	
Acetic acid 2·525 + 1·023	3·548	0·186
Methyl acetate	3·362	

* Since writing the above, determinations of the magnetic rotary power of propyl propionate and propyl formate have been made and added to this paper. Although perhaps not sufficiently examined to enable the matter to be spoken of as an established fact, yet it will be found that they do give lower numbers than the corresponding ethyl salts, making it probable that the line in Diagram VI for salts containing propyl and higher radicals should be lower than that for the ethyl salts by about 0·02 or 0·03.

DIAGRAM 7.
METHYL DISPLACEMENTS.

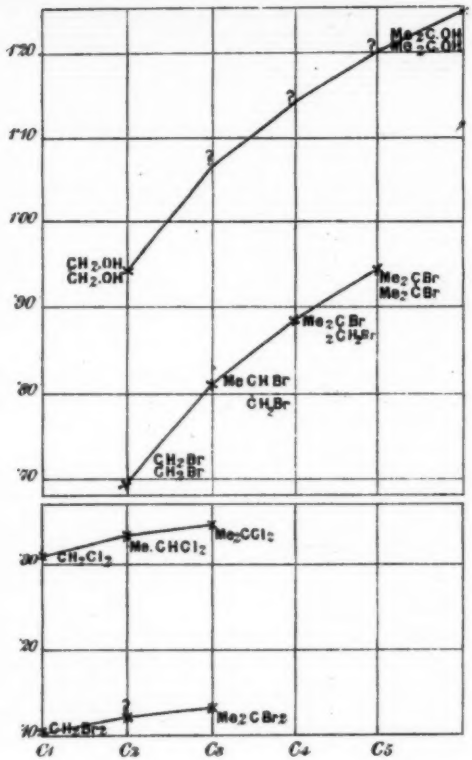


DIAGRAM 8.
HALOGEN RE-ARRANGEMENTS. WITH INCREASING CARBONS.

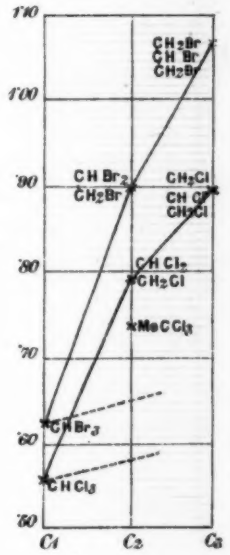


DIAGRAM 9.
NORMAL AND UNSATURATED.

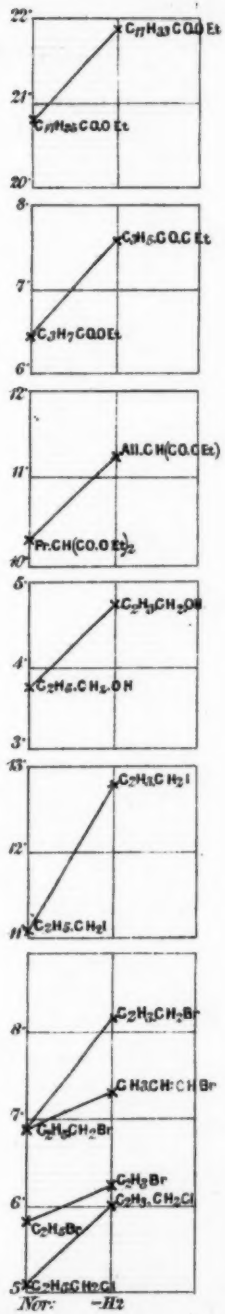
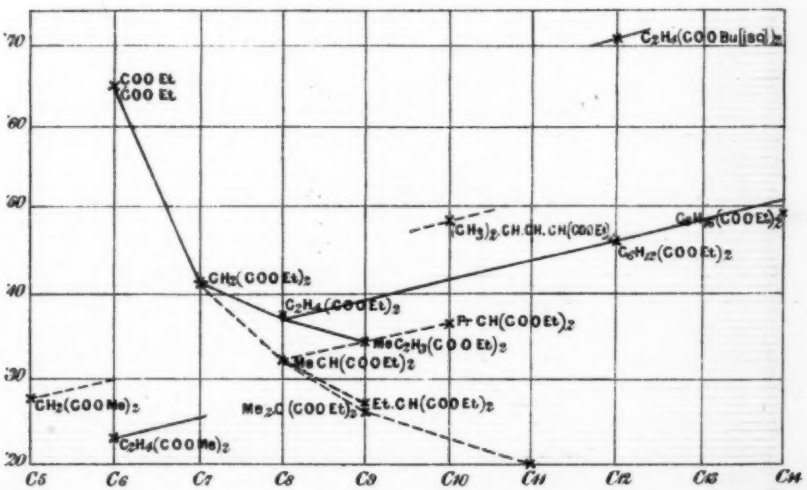


DIAGRAM 10.
$C_nH_{2n-2}O_4$ ETHEREAL SALTS.



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In Diagram VI lines have been drawn for the methyl parallel to those of the ethyl salts, but it will be noticed that the results found for methyl formate and methyl acetate do not quite agree with them; however, the difference is so small, that it is thought the variation may be due to errors of experiment, but as methyl salts give a much wider difference between the rotation and that of the acids they are prepared from than the ethyl salts do, it is possible that the two methyl salts in question should not be represented as following lines perfectly parallel to the ethyl salts.

In the homologous series we get—

Butyric acid 4·472 + 1·023.	5·495	0·108
Methyl butyrate.....	5·387	

and no doubt this is the difference which would be found for the methyl salts of all the fatty acids; the series constant for these is 0·273.

The further consideration of these methyl salts must be in relation to the ethyl salts, because it has reference to the oxalic series where the acids are solid, and therefore have not been examined. It will be found then that the methyl salts have a series constant 0·052 lower than the ethyl salts.

The acids of the oxalic series being dibasic, the displacement of the hydrogen in two hydroxyls by alcohol radicals would be expected to produce differences in the magnetic rotation about twice as large as is the case in monobasic acids.

Two comparable bodies have been examined. They are the ethyl and methyl salts of malonic and succinic acids. (See Diagram X.)

Ethyl malonate	7·410	0·084
Methyl malonate 5·280 + 1·023 × 2	7·326	
Ethyl succinate	8·380	0·103
Methyl succinate 6·231 + 1·023 × 2	6·277	
Mean		0·094
		= 0·047 × 2

Therefore the introduction of two methyls in place of the hydrogens of the hydroxyl of dibasic acids reduces the magnetic rotation to very nearly twice the extent which the introduction of one methyl does in the fatty series, a result which is quite consistent. It is however probable that the number being slightly lower is not accidental, but that the introduction of the second methyl has a somewhat smaller influence than the introduction of the first.

IV. Oxides.

The displacement of the hydroxylic hydrogen in alcohols by radicals appears to follow the same law as in acids. Thus ethyl oxide relatively differs from ethyl alcohol in the following way:—

Ethyl alcohol $2{\cdot}780 + 1{\cdot}023 \times 2$ ..	$4{\cdot}826$	$0{\cdot}049$
Ethyl oxide	$4{\cdot}777$	

This varies only 0·007 from that found in the case of the ethereal salts of the fatty acids. (See Diagram IV.)

Influence of the CO.OH*-group upon the Magnetic Rotation of Bodies.*

The rotation of this group is evidently high, but the remarkable fact connected with it, is that its influence is to cause reduction in the magnetic rotation of alcohol radicals when associated with it. Thus formic acid drops, allowing for difference of composition, 0·169, when its hydrogen is displaced by methyl so as to form acetic acid, and then again drops about 0·086 for an introduction of a methyl in place of hydrogen producing propionic acid. The influence is smaller if the hydrogen of the hydroxyl of the group COOH be displaced by ethyl so as to form $CO.OC_2H_5$: then the introduction of methyl into ethyl formate so as to produce ethyl acetate, reduces its molecular rotation by 0·125, and this is again reduced on being converted into ethyl propionate by 0·033. (See Diagram VI.)

On considering the molecular rotation of ethyl oxalate, it is found that the differences are about double what they are in the case of the monobasic acids. Thus, between ethyl oxalate and ethyl malonate there is a drop in the series constant of 0·269, which agrees closely with twice the difference between that of ethyl formate and ethyl acetate, and from ethyl malonate to ethyl succinate, a further drop of 0·053, which is a trifle less than twice the difference between ethyl acetate and ethyl propionate. The effect of this CO.OH group is very remarkable, as being the opposite to that of halogens or hydroxyl, which raise the series constant. In the series of ethereal salts of dibasic acids, it apparently carries its influence much further than in the series of salts of monobasic acids, so that the effect of the introduction into the methylene or ethylene of malonic and succinic ethereal salts either of methyl, ethyl or any other radical is continuously to reduce the rotary power of the compound. This is graphically represented on Diagram X, where it will be seen that the introduction of methyl into ethyl succinate so as to form ethyl pyrotartrate, lowers the series constant or relative rotation by 0·056.

It is this peculiar power of the CO.OH-group to reduce the rota-

tions of hydrocarbon radicals, especially of those in immediate union with it, that probably accounts for the low rotary power of isobutyric acid and its derivatives, and it is very remarkable, as already noticed, that directly the CH_2-group, acting apparently as a screen, is introduced between the CO.OH and the isopropyl, the rotations increase and give the usual numbers for iso-compounds.

Effect of the Displacement of Hydrogen by Hydroxyl.

In reference to this subject, the relationship of alcohols to the paraffins may first be considered, and heptane and heptyl alcohol, and isopentane and isoamyl alcohol may be taken as examples:—

Heptyl alcohol	7·850	0·181
Heptane	7·669	
Isoamyl alcohol (inactive)	5·959	0·209
Isopentane	5·750	

For other comparisons the calculated values of the paraffins must be employed:—

Propyl alcohol	3·768	0·191
Propane (calc.)	3·577	

The average of these three numbers is 0·194. Two different examples may be next examined, namely, glycol and glycerol:—

Glycol	2·943	0·389 = 0·194 × 2
Ethane (calculated) ..	2·554	
Glycerol	4·111	0·534 = 0·178 × 3
Propane (calculated) ..	3·577	

These numbers indicate that the influence of hydroxyl on the rotation gradually diminishes with successive groups, and that this is apparently the case will be seen from the circumstance that if the value for ethylic alcohol be subtracted from that for glycol, only 0·163 is left as representing the effect of the second hydroxyl group, leaving 0·226 for the first, but as ethyl alcohol is rather abnormal in its rotation, another comparison may be made. It has been seen that the average number representing the effect of the first introduction of hydroxyl into paraffins is 0·194; if this be taken from the value deduced from the comparison of propane with glycerol, it leaves 0·340 as the value of the effect of the second and third hydroxyls, which in their turn should not be equal in value, one being rather more, and the other rather less than $\frac{0·340}{2}$ or 0·170.

The influence of hydroxyl when displacing the hydrogen in alde-

hydes, and thus producing acids, is seen from the following comparisons:—

Acetic acid	2·525	0·140
„ aldehyde	2·385	
Propionic acid	3·462	0·130
„ aldehyde	3·332	
Isovaleric acid	5·635	0·148
„ aldehyde	5·487	
Œnanthylic acid	7·552	0·130
„ aldehyde	7·422	
Average		0·137

It is thus seen that both in the series of the paraffins and the aldehydes, the introduction of hydroxyl in place of hydrogen increases the molecular rotation; but in the latter case, the influence is somewhat smaller, due undoubtedly to the existence of CO in the compound. (See Diagram XIV.)

The Influence of Oxygen on the Magnetic Rotation of Bodies.

The subjects under the last two headings may also be considered from this point of view, as alcohols and acids differ in composition from paraffins and aldehydes by the addition of an atom of oxygen. But both in acids and aldehydes if considered as derived from paraffins, there is also a displacement of 2H by O. The influence of this kind of displacement may be best seen by comparing a paraffin and an aldehyde, thus:—

Heptane	7·669	0·247
Œnanthaldehyde	7·422	

This shows a great reduction, a result apparently the reverse of that produced by the addition of oxygen in the formation of a hydroxyl-group. But as we have to take into account the value of the two hydrogens removed (which, as is shown further on, amounts to about 0·508), it will be found that oxygen when displacing two hydrogens on the same carbon has nearly double the influence which it has when simultaneously combined with carbon and hydrogen.

Displacement of Hydrogen by Acetyl.

Two acetyl derivatives, viz., ethyl acetoacetate and ethyl acetosuccinate, have been examined. The following is a comparison of them with the non-substituted compounds:—

Ethyl acetoacetate.....	6·501	2·039
„ acetate.....	4·462	
„ acetosuccinate.....	10·343	1·963
„ succinate.....	8·380	

This amount is rather less than that required for an increase of $CH_2 \times 2 = 2{\cdot}046$, although acetyl contains methyl: no doubt a result due to the existence of CO in acetyl.

It will be seen that the influence of acetyl in the case of the acetosuccinate is about 0·07 lower than in the case of the acetoacetate. Until these bodies have been more critically examined, it would be premature to say whether this is really accidental or larger than it should be. The latter is thought to be the most likely.

Unsaturated Compounds.

I. Saturated Compounds — 2H.

The only hydrocarbon of the olefine series which has as yet been examined is amylene (trimethylethylene). The rotary power was found to be 6·121.

Now if we assume that the rotation of normal olefines differs from paraffins in the same way as allyl alcohol differs from propyl alcohol, the rotation of normal amylene will be 6·541. The existence of methyl groups in this body would therefore seem to reduce the rotation, and not raise it. This is very remarkable, but until other olefines have been examined, no reliable deductions can be made.

The difference between the magnetic rotation of the saturated and unsaturated compounds is very marked in the following examples:—

Ethyl crotonate or methacrylate.....	7·589	1·112
„ butyrate	6·477	
„ oleate	21·909	1·112
„ stearate (calc.)	20·797	
„ allylmalonate.....	11·281	0·914
„ propylmalonate	10·367	
Allyl alcohol.....	4·682	0·914
Propyl „	3·768	

These differences in rotation would make it very easy to determine whether a body be a saturated compound or not. It will be observed that monobasic acids give a somewhat larger difference than allyl alcohol and ethyl allylmalonate. The halogen derivatives will be considered further on. (See Diagram IX.)

II. Saturated Bodies — 4H.

One example of this kind has been studied, but a little doubt exists as to the purity of the specimen examined—it is—

Ethyl diallylmalonate	14·998	0·648
„ allylmalonate	11·281 + 1·023 × 3 = 14·350	

There can be no doubt that it shows that compounds of this nature have a considerably larger rotation than those of Group I just discussed.

Compounds containing the Halogens.

I. Chlorides of the Normal Alcohol Radicals.

The influence of chlorine on the magnetic rotations of bodies is to raise them considerably. The following normal compounds have been examined :—

Ethyl chloride	4·039
Propyl „	5·056
Octyl „	10·128

The ethyl chloride has not been examined so fully as could be wished. On account of its low boiling point very few opportunities suitable for its examination have occurred.

The rotation of the chlorides is about 1·480 higher than the corresponding paraffins, the series constant being 1·988, that of the paraffins, 0·508. (See Diagram XIII.)

II. Bromides of the Normal Alcohol Radicals.

These give higher rotations than the chlorides. The following results have been obtained :—

Methyl bromide.....	4·644
Ethyl „	5·851
Propyl „	6·885
Octyl „	12·025

Fresh determinations of methyl bromide would be desirable, though there is no reason to doubt the above, but they were made in the earlier days of this research. However, as it is necessary to work at about 0° C., the boiling point of the bromide being 4·7—5°, it has been impossible, owing to the mildness of the winter, to re-examine it. The rotation of this series is relatively 3·308 higher than the paraffins, its series constant being 3·816. (See Diagram XII.)

III. Iodides of Normal Alcohol Radicals.

The rotations of these bodies are very high:—

	Mol. rotation.
Methyl iodide.....	9·009
Ethyl „	10·075
Propyl „	11·080
Octyl „	16·197

The series constant is 8·011, or 7·503 higher than the paraffins. In this series it will be seen that iodide of ethyl is relatively slightly higher than propyl iodide, and it is thought quite probable that additional measurements of the chloride and bromide would show a similar difference, in relation to the corresponding propyl derivatives; the difference, however, is very small, but considering other series, it would still appear that the halogen compounds of ethyl do not strictly belong to the homologous series. (See Diagram XI.)

Influence of the Displacement of Hydrogen by Methyl in the Halogen Derivatives of the Normal Compounds.

Here a similar effect is produced upon the magnetic rotation to that observed in the previous instances which have been considered.

The following is a comparison between the normal-, iso-, and secondary halogen compounds:—

Chlorides.

	Mol. rotation.	Diff.
Isopropyl chloride.....	5·159	0·103
Normal propyl chloride	5·056	
Isobutyl chloride	6·144	0·064
Normal butyl chloride (calc.).....	6·080	
Isoamyl chloride	7·168	0·065
Normal amyl chloride (calc.).....	7·103	
Secondary octyl chloride.....	10·248	0·076
Normal octyl chloride (calc.).....	10·172	
Mean.....		0·077

Series constant.... 2·068.

Bromides.

Isopropyl bromide	7·003	0·118
Normal propyl bromide	6·885	
Isobutyl bromide	8·003	0·095
Normal butyl bromide (calc.)	7·908	
Isoamyl bromide	0·042	0·111
Normal amyl bromide (calc.)	8·931	
Mean		0·108

Series constant.... 3·924.

Iodides.

Isopropyl iodide	11·182	0·102
Normal propyl iodide	11·080	
Isobutyl iodide	12·199	0·096
Normal butyl iodide (calc.)	12·103	
Isoamyl iodide	13·200	0·074
Normal amyl iodide (calc.)	13·126	
Secondary hexyl iodide	14·229	0·080
Normal hexyl iodide	14·149	
Mean		0·088

Series constant .... 8·099.

In these tables, halogen derivatives of isopropyl have been admitted. This has been done as a matter of convenience, but it is doubtful whether they should be classified with the others, as they do not contain the CH_2-group, and it will be observed that the rotations given by them are slightly higher than in the cases of the other iso-bodies. (See Diagrams XI, XII, and XIII.)

The further introduction of methyl has only been examined in the case of the tertiary chloride and bromide of trimethylcarbinyl. This, however, causes, as in the case of the alcohols, another rise in rotary power, as the following comparisons show:—

Tertiary butyl chloride—Trimethyl carbinyl chloride	6·257	0·113
Isobutyl chloride	6·144	
Tertiary butyl bromide	8·238	0·235
Isobutyl bromide	8·003	

See Diagrams XII and XIII.

In the case of the alcohols, it was noticed that isopropyl alcohol (dimethylcarbinol) acted in an anomalous manner, giving differences in the rotation much higher than was expected. In the case of the

DIAGRAM 11.
IODIDES.

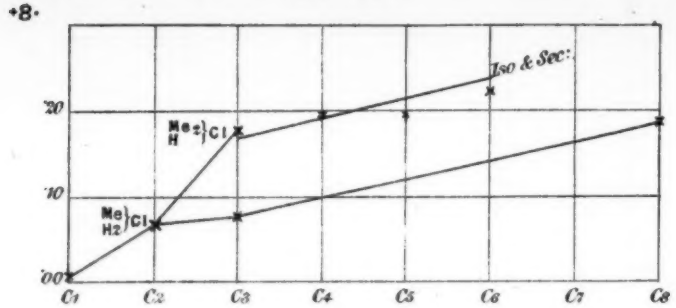


DIAGRAM 12.
BROMIDES.

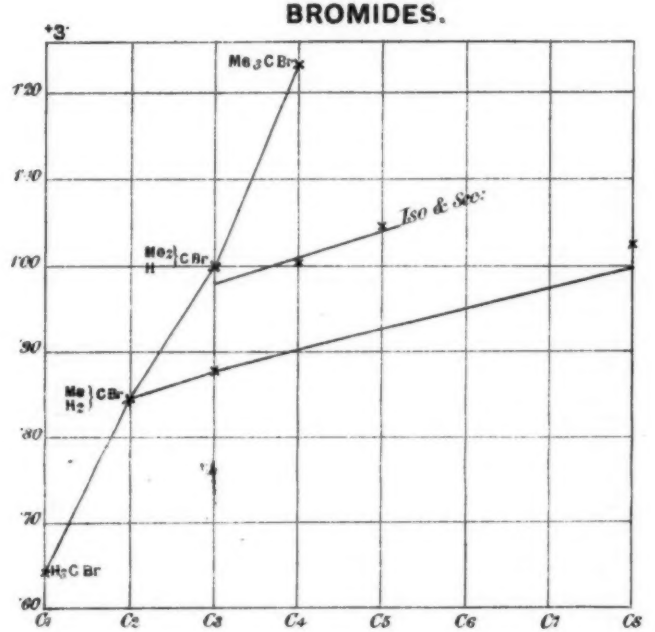


DIAGRAM 13.
CHLORIDES.

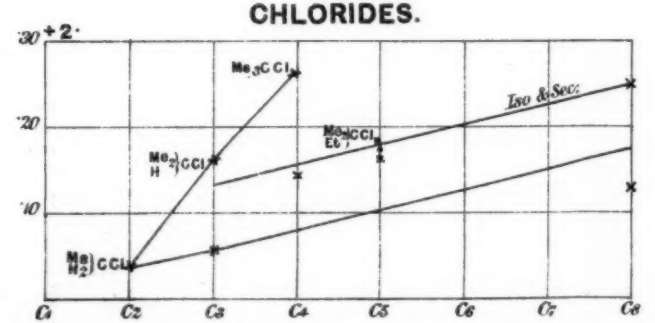


DIAGRAM 14.
HYDROXYL DISPLACEMENTS.

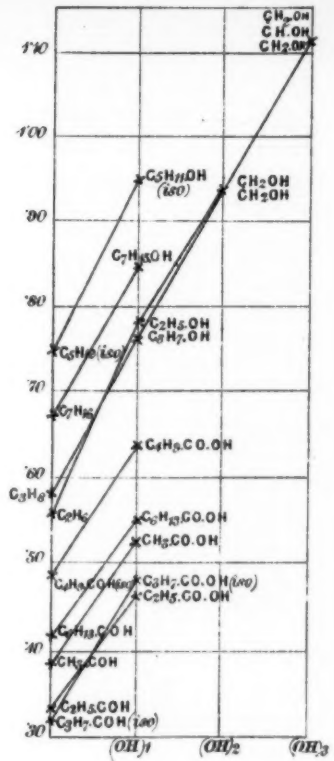


DIAGRAM 15.
CHLORINE DISPLACEMENTS.

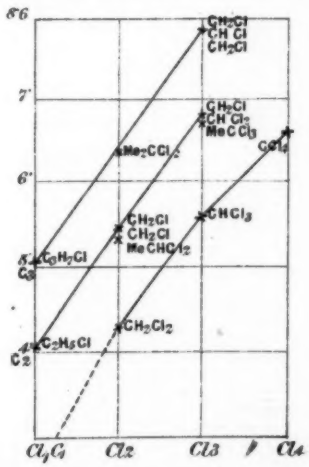


DIAGRAM 16.
BROMINE DISPLACEMENTS.

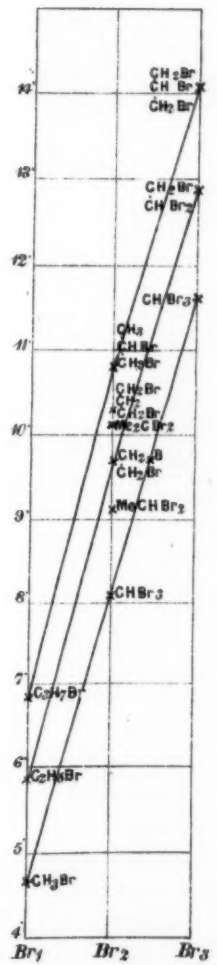
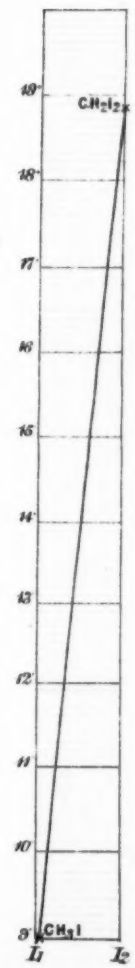


DIAGRAM 17.
IODINE DISPLACEMENTS.



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bromide, however, we get an anomaly of similar magnitude with trimethylcarbinol. On studying the numbers obtained from the foregoing halogen compounds, we find the iso and secondary bodies in the case of chlorides and iodides, not showing quite so great a difference from the normal as in the cases previously studied. The bromides, however, give a difference larger than the chlorides and iodides, and very nearly the same as other compounds. The diagrams will show these points. (See Diagrams IV, V, VI, and XI, XII, XIII.)

Influence of the Displacement of Hydrogen in Isopropyl Chloride by Ethyl.

It was noticed with tertiary amyl alcohol (dimethylethylcarbinol) that, viewed as an ethylisopropyl alcohol, the introduction of ethyl, instead of raising the rotation as methyl did, actually reduced it to a rotation about the same as a secondary or iso alcohol. The same thing is found with dimethylethylcarbinyl chloride, its rotation being nearly the same as isoamyl chloride.

Dimethylethylcarbinyl chloride	7·182	0·013
Isoamyl chloride	7·168	

See Diagram XIII.

Chlorine, Bromine and Iodine Substitution Derivatives of Monocarbon Compounds.

Chloride of methyl being a gas has of course not been examined. The following series have been examined, and their differences compared:—

Carbon tetrachloride	6·582	1·023
Chloroform	5·559	
Methylene chloride	4·313	1·246

Here it will be noticed that the introduction of chlorine, commencing with methylene chloride, does not cause the same change in rotation for every hydrogen-atom displaced, but that the influence becomes smaller between chloroform and carbon tetrachloride.

Bromoform	11·626	3·506
Methylene bromide	8·110	
Methyl bromide	4·644	3·466

In this case only a small difference is noticed, the introduction of the second atom of bromine producing a greater difference than that of the first.

Methylene iodide	18·827	9·818
Methyl iodide	9·009	

The influence of the second addition of iodine, it will be noticed, is considerably greater than the rotation of methyl iodide itself. Iodine acts like bromine, therefore, but more powerfully. (See Diagrams XV, XVI, and XVII.)

Effect of Introducing Methyl into Monocarbon Halogen Derivatives.

We have the following examples for comparison in this case :—

Chloracetol	6·344	1·009
Ethylidene chloride	5·335	
Methylene chloride	4·313	1·022
Bromacetol	10·137	1·037
Ethylidene bromide	9·100	
Methylene bromide	8·110	0·990

See Diagram VII.

Here we have a very remarkable result, the methyl group only having an influence similar to the addition of CH_2 in the homologous series. This has only been found to be the case with derivatives of monocarbon bodies, in which the two halogen-atoms are associated with the same carbon-atom. The only other case of this kind which has been examined is the following :—

Methyl-chloroform	6·740	1·181
Chloroform	5·559	

Subtracting the usual amount for difference of composition, viz., 1·023, we get 0·158 as the extra influence in this case, which is rather more than is found in iso-compounds. (See Diagram VIII.)

Chlorine and Bromine Substitution Derivatives of Dicarbon Compounds.

The following bodies have been examined, and are compared—

Monochlorethylene chloride	6·796	1·311
Ethylene chloride	5·485	
Ethyl chloride	4·039	1·446
Monobromethylene bromide	12·897	3·197
Ethylene bromide	9·700	
Ethyl bromide	5·851	3·849

We find here that the successive displacements produce lower effects, the diminution in the case of bromine compounds being very much greater than in that of the chlorine compounds. (See Diagrams XV and XVI.)

Methyl Derivatives of Ethylene Bromide.

The following have been examined :—

Trimethylethylene bromide—isoamylene bromide	12·947	1·057
Dimethylethylene bromide—Isobutylene bromide	11·890	1·070
Monomethylethylene bromide—Propylene bromide	10·820	1·120
Ethylene bromide	9·700	

Deducting 1·023 from each of these, the special rise in the rotation for each methyl group will be arrived at:—

$$1{\cdot}057 - 1{\cdot}023 = 0{\cdot}034$$
$$1{\cdot}070 - 1{\cdot}023 = 0{\cdot}047$$
$$1{\cdot}120 - 1{\cdot}023 = 0{\cdot}097$$

We here again have an instance where successive displacements reduce the influence of the group introduced. The above numbers when represented graphically form a curve. (See Diagram VII.)

Chlorine and Bromine Derivatives of Tricarbon Compounds.

The following have been examined, and are compared :—

Trichlorhydrin	7·897	2·841 = 1·420 × 2
Propyl chloride	5·056	
Tribromhydrin	14·068	3·248
Propylene bromide	10·820	
Propyl bromide	6·885	3·935

Trimethylene bromide gives a rotation lower than propylene bromide by 0·479; the rotation is 10·341. This may be partially due to the fact that propylene bromide contains methyl; the difference, however, is large. (See Diagrams XV and XVI.)

Influence of Distribution of Halogens in Compounds.

The following comparisons are given of trichloro- and tribromo-compounds where the distribution of the halogens varies with each increase of carbon. (See Diagram VIII.)

		CH_2.
Chloroform	5·559	1·237 − 1·023 = 0·214
Chlorethylene chloride..	6·796	
Trichlorhydrin	7·897	1·101 − 1·023 = 0·078
Bromoform	11·626	1·271 − 1·023 = 0·248
Bromethylene bromide..	12·897	
Tribromhydrin	14·068	1·171 − 1·023 = 0·148

It will be seen that change of distribution in these cases causes a considerably greater difference in the rotation than results from the change of composition of CH_2 alone, and that the rotation increases with the increase of distribution.

Influence of the Combination of Chlorine with Vinyl Bromide.

Vinyl bromide and its methyl-derivative bromopropylene, as is noticed under the next heading, have very low rotations, considering that they are unsaturated bodies. The former, however, when combined with chlorine, becomes a saturated body, and the increase of rotation is greater than that ordinarily caused by the addition of chlorine. Unfortunately no analogous body has been examined to compare it with.

Unsaturated Halogen Derivatives.

Examples of two series have been examined which show remarkable differences in their molecular rotations. They are the vinyl and allyl series.

I. Vinyl Series.

Vinyl bromide, $CH_2:CHBr$	6·220	0·369
Ethyl bromide	5·851	
Bromopropylene, $CH_3.CH:CHBr$, *i.e.* methylvinyl bromide	7·295	0·410
Propyl bromide	6·885	

II. Allyl Series.

Allyl chloride.....	6·008	0·952
Propyl „	5·056	
Allyl bromide	8·221	1·336
Propyl „	6·885	
Allyl iodide	12·788	1·708
Propyl „	11·080	

Here we get the very curious result that the bromides of vinyl and methylvinyl give rotations which differ from the normal series by

only 0·390, whereas the bromide of allyl varies by nearly $3\frac{1}{2}$ times that amount, viz., 1·336.

It is interesting to notice that the difference between the halogen-compounds of normal and unsaturated bodies is not the same for all the halogens, as in other series, but increases in the same direction as the atomic weight of the halogens. (See Diagram IX, lower half.)

Observations on Ethyl Malonate and its Derivatives, and also on Ethyl Acetoacetate.

Much labour has been spent on the examination of the derivatives of ethyl malonate. Some of these derivatives have been referred to: the following is a list of those which have not yet been considered:—

Ethyl methylmalonate (isosuccinate)	8·326
Ethyl dimethylmalonate.....	9·268
Ethyl ethylmalonate	9·272
Ethyl diethylmalonate.....	11·197

Of these bodies, it will be observed that the dimethyl- and ethyl-malonic salts give practically the same rotation. This is analogous to what we find in the series of monobasic acids where dimethylacetic (isobutyric) acid and ethylacetic (butyric) acid give practically the same numbers. It was expected that ethyl ethylmalonate would be the first member of a series of homologous bodies, and that ethyl propylmalonate would be the second, but this latter compound has a rotation, allowing for change of composition, 0·072 higher. The rotation of ethyl diethylmalonate is considerably lower than that of the monoethyl derivative, allowing for change of composition; whether this is still due to the reducing influence of the two carboxyl-groups it is impossible to say at present. No rotations corresponding to those of the homologous series have been found as yet for the derivatives of ethylmalonate, and before anything definite can be said respecting this series, fresh facts must be accumulated. (See Diagram X.) Comparative experiments with ethyl acetoacetate and its derivatives would be interesting in connection with this subject, because there is some reason for believing that its derivatives would act in a similar manner to those of ethyl malonate. For example, rotation in ethyl allylacetoacetate differs from that of ethyl acetoacetate to very nearly the same extent as ethyl allylmalonate differs from ethyl malonate—

Ethyl allylacetoacetate.....	10·382	3·881
Ethyl acetoacetate.....	6·501	
Ethyl allylmalonate	11·281	3·871
Ethyl malonate	7·410	

On subtracting 1·023 × 3 from these numbers to allow for difference of composition they become 0·812 and 0·802 respectively, which is a smaller difference than is generally found between the saturated and unsaturated series, or between ethyl propyl- and allyl-malonates. This similarity between these allyl-derivatives makes it very probable that ethyl propylacetoacetate would differ from ethyl acetoacetate just as ethyl propylmalonate differs from ethyl malonate, and in fact that it would, as already stated, yield derivatives behaving, in reference to their rotation, in the same way as the derivatives of ethyl malonate.

Observations on the Succinic Series.

Judging from the examination of the ethereal salts of this series, succinic acid would appear to be the first member of the homologous series, whereas from what has been said in other parts of this paper, glutaric acid should be the first member, as it contains a CH_2-group unassociated with carboxyl. Unfortunately I have not had this acid to examine. I still think, however, that it will be found to occupy that position, but that the series constants of both it and succinic acid are very close to each other; as it is, the series constant of ethyl succinate is slightly higher than that of ethyl suberate and sebate. In the diagram, however, I have assumed them to be equal, as the difference is but small. (See Diagram X.)

Unsaturated Dibasic Acids.

Ethyl citraconic and mesaconic have been measured again, but the numbers are not given in this paper, as the study of these compounds and of other unsaturated acids will, it is hoped, form a separate communication; their rotation is considerably higher than the corresponding saturated compounds.

Derivatives of Ethylene and Ethylidene Glycols.

The following products have been examined:—

Ethylene acetate	6·454
Ethylene propionate	8·318
Dimethyl acetal	4·647
Diethyl acetal	6·968

Unfortunately there are no other bodies which have as yet been examined with which these can be compared; the numbers they give, however, appear to be consistent, judging from the rough comparisons which follow—

Ethylene acetate	6·454	3·511
Glycol	2·943	

This difference indicates the effect produced by displacing the two hydroxyl hydrogens by acetyl. The effect of one is therefore 1·755.

Propyl acetate	5·487	1·719
Propyl alcohol	3·768	

This difference does not greatly vary from the above.
The next comparison is the propionate of ethylene—

Ethylene propionate	8·318	5·375
Glycol	2·943	

This is the influence produced by displacing two hydroxyl hydrogens by propionyl; or 2·687 for one displacement—

Propyl propionate* (calc.)	6·475	2·707
Propyl alcohol	3·768	

This difference corresponds closely with the above.

With the acetals or ethers (oxides) of ethylidene glycol, rough comparisons may also be made. It has been seen that when an acid is converted into a methyl salt, its series constant is reduced by 0·108, and for an ethyl salt by 0·056. The difference from alcohol to ethyl oxide gave a reduction of 0·049, and it is evidently more consistent to take this number, as the comparison is between an oxide and an alcohol, but for the methylic compound there is no other choice than the above. To find then the value of ethylidene glycol, it will be necessary to subtract from its ether the rotation for the difference of the composition, and then add twice one of the above numbers, according to the product under consideration, to bring back the rotation from that of an ether to that of an alcohol, thus:—

Methyl acetal	4·647	
$CH_2 \times 2 = 1·023 \times 2$	2·046	
	2·601	
0·108 × 2	0·216	
	2·817	Ethylidene glycol?
Ethyl acetal	6·968	
$CH_2 \times 4 = 1·023 \times 4$	4·092	
	2·876	
0·049 × 2	0·098	
	2·974	Ethylidene glycol?

* With the measurements recently made of propyl propionate it is as follows:—

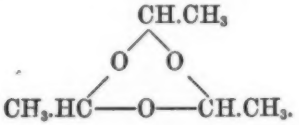
Propyl propionate	6·429	2·661
Propyl alcohol	3·768	

The last number is very near to that of glycol; but if there be a difference between ethylene and ethylidene glycols, similar to that which exists between ethylene and ethylidene chlorides, the first is very nearly correct.

These rough deductions are sufficient to show that there is very little reason to doubt that the derivatives of these glycols are quite consistent with other bodies in regard to their magnetic rotation, and that all that is wanted to prove this, is more closely allied products for comparison.

Paraldehyde.

This substance may be regarded as an oxide of ethylidene:—



Its molecular rotation is 6·662. There are no substances at present examined with which this can be compared, in order to test the correctness of the above view of its constitution.

Magnetic Rotary Power of the Elements when in Combination.

If the molecular rotary value which has been found for CH_2 (viz., 1·023), when in combination with other groups, be subtracted from that of a paraffin as many times as the latter contains carbon-atoms, a remainder will be obtained representing the value of 2H, thus:—

Heptane	7·669
$CH_2 \times 7 = 1{\cdot}023 \times 7$.....	7·161
	0·508 = 2H

Also if the value of a paraffin containing an even number of carbon-atoms be divided by 2, the product should represent the value of an alcohol radical, thus:—

Hexane = 6·646 ÷ 2 = 3·323, which is the value of propyl, and if this be subtracted from a corresponding paraffin, we again get a value for hydrogen = 0·254.

Now if we take from the value of CH_2 that of 2H, we should get that of C = 0·515.

Having obtained these results, values for the halogens can be obtained, thus:—

Propyl chloride ..	5·056	1·733
Propyl	3·323	
Propyl bromide ..	6·885	3·562
Propyl	3·323	
Propyl iodide	11·080	7·757
Propyl	3·323	

The influence of hydroxyl displacements in the paraffins has already been considered, and this, as previously noticed, may be taken as a value for oxygen, which in this case is 0·194. In the hydroxyl of acids its value is however 0·137.

Oxygen, when displacing 2 atoms of hydrogen in a carbon-compound so as to form carbonyl is, however, different; by this replacement it reduces the value of the compound by 0·247, which means that its value is that much less than 2H, or 0·261 under those circumstances. This is consistent with the observation respecting the refractive powers of bodies where oxygen in this kind of combination, and also carbon in unsaturated bodies, has a distinct second value.

These values, as a matter of course, work very well when used for the series of compounds from which they have been deduced; but when applied to other homologous series, give only approximate results. That this should be so is evident: for example, it has been found that the substitution of hydrogen in a radical by methyl increases its rotation more than should result from change of composition. The acids and ethereal salts also which have the same composition have different rotary powers. Again, these values will not fit in for formic, acetic, and oxalic acids or their ethereal salts, &c.

Oxygen, as in hydroxyl in alcohols, gives a value 0·194, but in acids 0·137. With the halogen-compounds it is seen that the molecular rotation changes with successive displacements (as in carbon tetrachloride), with radicals containing different numbers of carbon-atoms, and with differences of distribution, &c., and the higher the atomic weight of the halogen, the greater are the variations. These facts when compared with fresh results will probably be of considerable importance. The variations of the magnetic rotations of substances are evidently due to differences in the molecular arrangements of the elements they contain, as well as to their composition. This is one of the most interesting points connected with this inquiry, no other physical properties of bodies yet examined showing this in such a marked manner, and it is believed that the examination of the magnetic rotation of bodies will be of considerable value to chemists in helping them to come to conclusions as to the constitution and composition of compounds under examination. In the following table the formulæ are given by which the magnetic rotation of bodies

belonging to twenty-six series can be calculated, it is believed in most cases with considerable accuracy. Any errors in the series constants which are deduced from the examination of one example will probably not exceed more than 0·01 to 0·03 :—

Formulæ for Calculating the Molecular Magnetic Rotation of Bodies of the Homologous Series.

		Series constant.
Paraffins	C_nH_{2n+2} =	0·508 + n(1·023)
„ iso	„	0·621 „
Alcohols	$C_nH_{2n+2}O$	0·699 „
„ iso and sec.	„	0·844 „
Oxides	„	0·642 „
„ iso	„	0·932 „
Aldehydes	$C_nH_{2n}O$	0·261 „
„ iso, and ketones	„	0·375 „
Acids	$C_nH_{2n}O_2$	0·393 „
„ iso	„	0·509 „
Formic ethereal salts (ethyl, and above)	„	0·495 „
Acetic ethereal salts (ethyl, and above)	„	0·370 „
Ditto, iso	„	0·485 „
Methyl salts	„	0·273 „
Ethyl salts and above	„	0·337 „
Ditto, iso	„	0·449 „
Methyl salts, succinic series		0·093 „
Ethyl salts, succinic series	$C_nH_{2n-2}O_4$	0·196 „
Ditto, iso	„	0·422 „
Chlorides	„	1·988 „
„ iso and sec.	$C_nH_{2n+1}Cl$	2·068 „
Bromides	„	3·816 „
„ iso and sec.	$C_nH_{2n+1}Br$	3·924 „
Iodides	„	8·011 „
„ iso and sec.	$C_nH_{2n+1}I$	8·099 „
Ethyl salts, unsaturated	$C_nH_{2n-2}O_2$	1·451 „

There are other points connected with this paper such as the difference in rotation between saturated and unsaturated compounds, methyl derivatives, &c., which might be summarised, but in the present state of the inquiry it is perhaps best to leave them as they are in the body of this paper. There are many other series of bodies containing other elements than those referred to in this paper, which require examination. Several of these I am making arrangements to commence the study of, such as nitrites and the nitro-compounds, also the nitrates. The subject of physical isomerides, which was the cause of my commencing the study of the magnetic rotation of bodies, is also in hand, as well as the series of aromatic compounds.

A list of the compounds examined is appended with their molecular

rotation, and the number of the pages where they are referred to in this paper.

I cannot conclude this communication without giving my best thanks to my assistant, Dr. L. T. Thorne, for the interest he has taken in this investigation, the suggestions he has made, and the patience and care with which he has helped me to carry it out.

	Molecular rotation.	Page.
Acids.		
Acetic	2·525	481, 545, 547, 556, 558
Butyric	4·472	483, 547, 552
„ iso	4·479	487, 547, 552
Caprylic	8·565	485, 547
Formic	1·671	480, 545, 547, 556, 558
Nonylic, pelargonic	9·590	486, 547
Œnanthylic	7·552	484, 547
Propionic	3·462	481, 547, 556, 558
Valeric	5·513	483, 547
„ iso	5·635	488, 547, 551
Alcohols.		
Allyl	4·682	536, 561
Amyl, iso (active)	5·943	469, 550
„ „ (inactive)	5·959	470, 550, 559
„ tertiary	5·987	471, 554
Butyl, iso	4·936	468, 550
„ tertiary	5·122	468, 554
Ethyl	2·780	465, 554
Heptyl	7·850	471, 548, 559
Methyl	1·640	465, 554
Octyl	8·880	472, 548
„ secondary	9·004	473, 553
Propyl	3·768	466, 548, 559, 571
„ iso	4·019	467, 553, 554
Polyhydric Alcohols and their Salts.		
Glycol	2·943	504, 559, 570
Glycerol	4·111	507, 559
Pinacone	7·245	506, 555
Ethylene acetate (glycol acetate)	6·454	505, 570
„ propionate	8·318	505, 571
Aldehydes.		
Acetic	2·385	475, 554, 560
Œnanthylic	7·422	477, 549, 560
Propylic	3·332	476, 549, 560
Isobutyric	4·321	476, 552
Isovaleric	5·487	477, 551, 554, 560
Paraldehyde	6·662	479, 572

	Molecular rotation.	Page.
Ethereal Salts of Monobasic Acids.		
Cetyl acetate	18·772	497, 547, 579
Ethyl acetate	4·462	491, 544, 547, 556
„ allylacetoacetate	10·382	540, 569
„ acetoacetate	6·501	493, 561, 569
„ butyrate	6·477	499, 547
„ „ iso	6·479	500, 547, 552
„ caproate	8·509	501, 547
„ α-crotonate	7·589	536, 549, 561
„ formate	3·564	489, 545, 547, 556
„ nonate (pelargonate)	11·571	503, 547
„ œnanthate	9·541	502, 547
„ oleate	21·909	537, 549, 561
„ propionate	5·452	496, 547, 556
„ valerate, iso	7·615	500, 551
Isobutyl acetate	6·623	495, 551
Isopropyl propionate	6·595	498, 553
Methyl acetate	3·362	493, 544, 556
„ butyrate	5·387	499, 557
„ formate	2·495	490, 544, 556
Octyl acetate	10·601	495, 547
Heptyl œnanthate	14·655	503, 544, 547
Propyl acetate	5·487	494, 544, 547, 571
„ formate	4·534	491
„ propionate	6·429	497, 544, 571
Ethereal Salts of Dibasic Acids.		
Ethyl acetosuccinate	10·343	517, 561
„ allylmalonate	11·281	538, 561, 569
„ diallylmalonate	14·998	538, 562
„ diethylmalonate	11·197	[illegible], 569
„ dimethylmalonate	9·268	511, 569
„ ethylmalonate	9·272	512, 569
„ isopropylmalonate	10·482	514, 551
„ malonate	7·410	508, 557, 569
„ methylmalonate (isosuccinate)	8·326	510, 569
„ methylsuccinate (pyrotartrate)	9·347	516, 558
„ oxalate	6·654	508, 557, 558
„ propylmalonate	10·367	514, 551, 569
„ sebate	14·496	518, 549
„ suberate	12·461	517, 549
„ succinate	8·380	515, 549
Isobutyl succinate	12·707	519, 551
Methyl malonate	5·280	509, 557
„ succinate	6·232	516, 557
Ethyl citraconate and mesaconate	—	570
Ketones.		
Acetone	3·514	478, 554
Methyl-propyl ketone	5·499	479, 554
Olefine.		
Amylene	6·121	448, 561

	Molecular rotation.	Page.
Oxides.		
Amyl, iso	11·168	474, 551
Ethyl	4·777	474, 558
Diethyl-acetal	6·968	507, 570
Dimethyl „	4·647	506, 570
Paraffins.		
Diisopropyl	6·784 ?	448
Heptane	7·669	447, 548
Hexane	6·670	446, 548
„ iso	6·769	447, 550
Pentane	5·638	445, 548
„ iso	5·750	446, 550
HALOGEN COMPOUNDS.		
Bromides.		
Allyl	8·221	542, 568
Amyl, iso	9·042	458, 564
Butyl „	8·003	457, 564
„ ter.	8·238	457, 564
Ethyl	5·851	455, 562, 566
Methyl	4·644	454, 562, 565
Octyl	12·025	458, 549, 562
Propyl	6·885	455, 549, 562
„ iso	7·003	456, 564
Bromopropylene, $CH_3.CH:CH.Br$	7·295	542, 568
Vinyl	6·220	540, 568
Dibromides.		
Amylene, iso	12·947	526, 567
Butylene „	11·890	525, 567
Ethylene	9·700	520, 566, 567
Ethylidene	9·100 ?	522, 566
Methylene	8·110	519, 565, 566
Propylene	10·820	523, 567
„ (bromacetol)	10·137	524, 566
Trimethylene	10·341	525, 567
Tribromides.		
Bromoform	11·626	533, 565, 568
Monobromethylene bromide (vinyl tribromide)	12·897	534, 566, 568
Tribromhydrin (allyl tribromide)	14·068	535, 567, 568
Chlorides.		
Allyl	6·008	541, 568
Amyl, iso	7·168	452, 563
„ ter.	7·182	452, 565
Butyl, iso	6·144	451, 563
„ ter.	6·257	451, 564

	Molecular rotation.	Page.
Chlorides (continued).		
Ethyl	4·039	449, 562, 566
Octyl	10·128	453, 549, 562
„ sec.	10·248	454, 563
Propyl	5·056	450, 549, 562, 567
„ iso	5·159	450, 563
Dichlorides.		
Ethylene	5·485	528, 566
Ethylidene	5·335	528, 566
Methylene	4·313	527, 565, 566
Propylene (chloracetol)	6·344	529, 566
Trichlorides.		
Chloroform	5·559	530, 565, 566, 568
Methyl chloroform	6·740	531, 566
Monochlorethylene chloride, (vinyl trichloride)	6·796	531, 566, 568
Trichlorhydrin, (allyl trichloride)	7·897	532, 567, 568
Carbon tetrachloride	6·582	532, 565
Iodides.		
Allyl	12·788	543, 568
Amyl, iso	13·200	462, 564
Butyl „	12·199	462, 564
Ethyl	10·075	460, 563
Hexyl, sec.	14·229	463, 564
Methyl	9·009	459, 563, 565
Octyl	16·197	463, 549, 563
Propyl	11·080	460, 549, 563
„ iso	11·182	461, 564
Methylene iodide	18·827	464, 565
Bromethylene dichloride	10·995	535

Cetyl Acetate.—Krafft has recently stated (*Ber.*, **17**, 1627) that ordinary cetyl alcohol contains octadecyl alcohol. My observations also show that it is not a pure substance. On first examining cetyl acetate, I prepared it from the ordinary alcohol (from Kahlbaum) and acetic anhydride, and did not fraction the product; it had a higher density and lower magnetic rotatory power than the substance to which the numbers on p. 497 refer. On fractioning it under reduced pressure, only about one-third was found to boil within the limits given, the temperature gradually but slowly rising. As the fractioning was very carefully carried out, it is believed that the substance finally examined was pure, or nearly so.

APPENDIX.

Method of Calculating Results.

As will be seen on reference to the beginning of this paper (p. 421), the formula for calculating the molecular rotation of a substance is—

$$\text{Mol.R.} = \overset{\text{Substance.}}{\frac{r \times Mw}{d}} \div \overset{\text{Water.}}{\frac{r' \times Mw'}{d'}} = \frac{r \times Mw \times d'}{r' \times Mw' \times d},$$

but as d' is always taken as the unit of reference in the densities employed in this paper, it may be eliminated from the above formula, which then becomes—

$$\frac{r \times Mw}{r' \times Mw' \times d}.$$

In practice it has been found advantageous to divide the calculation into two stages, as follows:—

$$\text{I. } \frac{r}{r'} = \text{Sp. R.} \qquad \text{II. Sp. R.} \times \frac{Mw}{Mw' \times d} = \text{Mol. R.}$$

Working in this way, the actual calculations necessary to obtain the results of the example (cetyl acetate) given on p. 438, are as follows:—

II.

Subs.	log 33·45	= 1·52440	
Water	„ 32·595	= 1·51315.	
		0·01124	= 1·0262 Sp. R.
		1·26187	
$t = 22°$		1·27310.	= 18·755 Mol. R.

III.

Subs.	log 33·38	= 1·52349	
Water	„ 32·50	= 1·51188.	
		0·01160.	= 1·0271 Sp. R.
		1·26151	
$t = 21°$		1·27311.	= 18·755 Mol. R.

IV.

Subs.	log 33·35	= 1·52310	
Water	„ 32·44	= 1·51108	
		0·01202	= 1·0280 Sp. R.
		1·26115.	
$t = 20°$		1·27317	= 18·757 Mol. R.

V.

Subs.	log 33·35	= 1·52310	
Water	„ 32·36	= 1·51001	
		0·01309	= 1·0306 Sp. R.
		1·26080	
$t = 19°$		1·27389	= 18·789 Mol. R.

Mol. wt. of subs.	log 284		= 2·45332
Mol. wt. of water	„ 18		= 1·25527.
$d\frac{22°}{22°}$ of subs.*	„ 0·86333		= $\bar{1}$·93618
			1·19145
			1·26187
	log 284		= 2·45332
	„ 18		= 1·25527.
$d\frac{21}{21°}$ of subs.	„ 0·86404		= $\bar{1}$·93653.
			1·19181
			1·26151
	log 284		= 2·45332
	„ 18		= 1·25527.
$d\frac{20°}{20°}$ of subs.	„ 0·86475		= $\bar{1}$·93689
			1·19216.
			1·26115.
	log 284		= 2·45332
	„ 18		= 1·25527.
$d\frac{19°}{19°}$ of subs.	„ 0·86546		= $\bar{1}$·93725
			1·19252
			1·26080

* The relative densities of the cetyl acetate at the temperatures of observation are of course calculated with the help of the coefficient of change of density deduced from the two relative density determinations given in the body of the paper.

XLVIII.—*Gas Analysis under Greatly Diminished Pressure.*

By Lothar Meyer and Karl Seubert.

Bunsen's method of gas analysis is so simple and accurate, that it seems scarcely possible to improve it. In the analysis of gases rich in hydrocarbons, however, such as have now frequently to be made in the laboratory, the atmospheric air, which has to be added to moderate the violence of the explosion, causes some inconvenience, and, moreover, is liable to affect the accuracy of the results, since it is difficult to hit the point at which all the combustible gas shall be completely burned without oxidising any of the nitrogen.

It is well known that the energy of combustion of explosive gaseous mixtures can be greatly moderated by diminishing the pressure, so much so indeed, that they may even become incapable of being ignited. Davy has shown (*Phil. Trans.*, 1817) that when the pressure of the oxyhydrogen mixture is reduced to $\frac{1}{18}$th, it no longer explodes. The application of this principle for the purposes of gas analysis has indeed been attempted of late years, but has not been generally adopted, on account of the complicated nature of the apparatus.

In 1869 McLeod (this Journal, **22**, 320) described a gas analysis apparatus in which the violence of explosion of the gaseous mixture was moderated by diminishing the pressure. In 1879 T. W. Thomas (this Journal, 1879, Trans., **35**, 213) determined the pressure for a number of combustible gaseous mixtures at which the explosion was harmless, and observed that the rarefaction produced by diminution of pressure was more effective in weakening the force of explosion than dilution with an indifferent gas; a result fully confirmed by our own observations. In the paper referred to, the author only gives a few analyses of methane, but had analysed other gases with satisfactory results.

The ease with which any pressure between 0 mm. and the ordinary atmospheric pressure may be obtained by Schoop's apparatus (*Inaug. Diss.*, Tübingen, 1880; *Ann. Phys. Chem.*, 1881, **12**, 550), induced us to apply it to gas analysis by explosion under diminished pressure, in place of the usual method of diluting it with an indifferent gas. The method proved to be not only easy to carry out and fairly accurate, but is safe and rapid.

The apparatus employed is a simplified modification of that described by Schoop (*loc. cit.*). Instead of the tube for vapour-density determinations, a eudiometer E, Fig. 1, is fixed in the mercury trough, and instead of the tube DE of the original drawing, there is a

barometer tube B, which is joined at the upper end to a capillary tube bent parallel to the barometer tube, and reaching nearly to the bottom of the trough.* The barometer B of Schoop's apparatus is suppressed. The barometer tube B is screwed by means of an iron nipple into the cast-iron bottom of the mercury trough W, and the eudiometer tube E, which is about 400 mm. long, is fastened in a similar manner by a turned iron plug. The arrangement of the iron plug, which is held fast by a bayonet-joint, is given in Fig. 2, and is fully described in Schoop's memoir. The tubes B and E, when in place, communicate by means of a horizontal perforation in the bed of the trough, into which the glass tube *g* is cemented; this is bent downwards at right angles, and passing through a perforation in the table T, reaches nearly to the floor. The lower end of the tube *g* is connected by means of a strongly covered caoutchouc tube with the mercury reservoir Q, which is placed on a wooden traveller, capable of moving vertically on the upright L. The reservoir can be raised or lowered at pleasure by means of a cord passing over the pulley L. The barometer tube is divided into millimetres and screws firmly into the base of the trough, the screw being lubricated so as to make it fit perfectly air-tight.

If, as is usually the case, moist gases have to be analysed, a few drops of water should be introduced into the barometer, either before it is screwed into its place or afterwards. In the latter case, the eudiometer tube E must be removed and the mercury reservoir Q lowered until the mercury has run out of the trough so far as to leave the end of the capillary tube uncovered. A small vessel of water, such as a crucible, is then placed under the capillary tube, so that the end of it may dip into the water, and the eudiometer E filled with mercury is again put in its place. The reservoir is now raised to expel some of the air, and then lowered so as to suck in part of the water, which is carried down by the current of air through the "Bunte's tube" *s*, which is sealed in the barometer tube about 10 cm. from the bottom. When the reservoir is again raised, a part of the water is retained here, whilst the excess is driven out with the air through the capillary tube. By repeatedly raising and lowering Q, the air may be entirely driven out of B. In this way, the sides of the tube are wetted sufficiently to render correction for the vapour-tension of water unnecessary.

The eudiometer, after it has been moistened with a drop of water, is filled with mercury in the usual manner as described by Bunsen. When it is fixed in its place, the pressure is gradually diminished, so as to detach any gas-bubbles adhering to the glass, and they are

* Similar to that employed by W. Hempel, "Neue Methoden zur Analyse der Gase," Braunschweig, 1880, p. 92, &c.

Fig 2.

Fig 1.

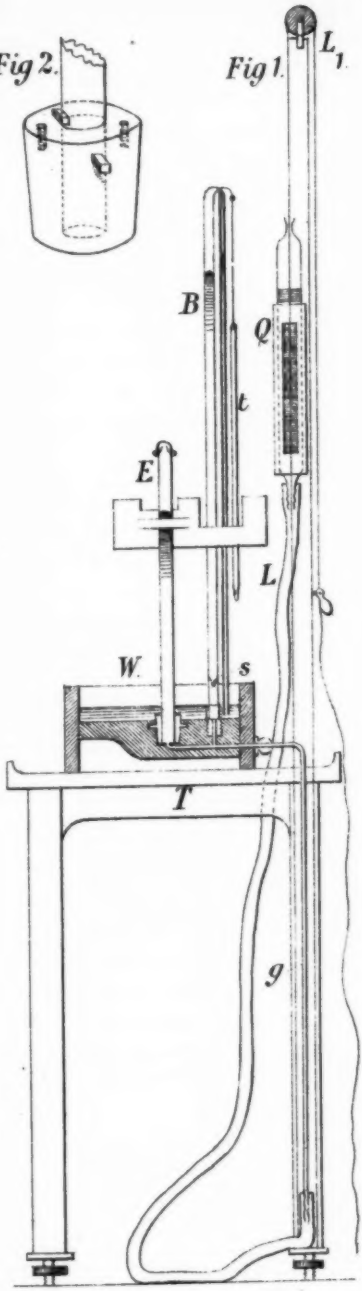
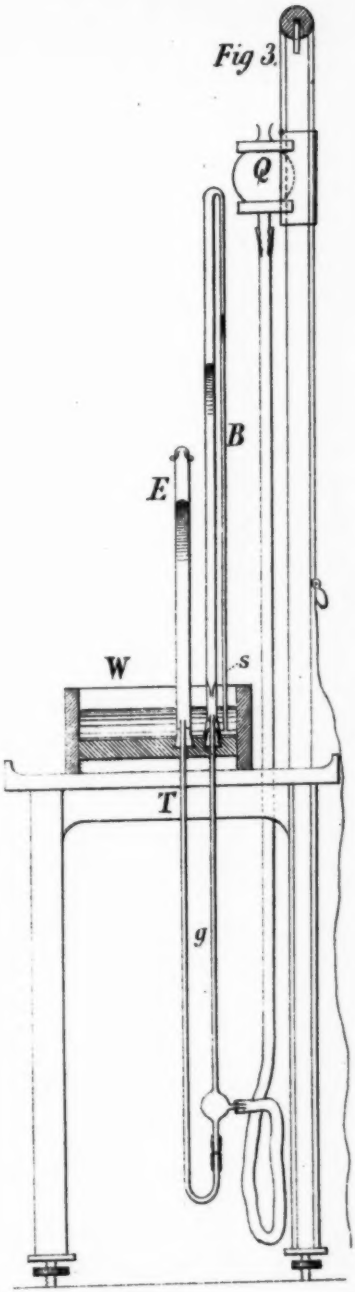


Fig 3.



Harrison & Sons, Lith., 3, Martin's Lane, W.C.

then driven to the top of the tube by again raising Q; if any air-bubbles are then visible near the wires of the eudiometer, Q is lowered so as to bring the mercury in the reservoir on a level with that in the trough, and they are removed by taking out the eudiometer and inverting it in the usual way.

Explosiveness of Gaseous Mixtures under Diminished Pressure.

It seemed advisable, first of all, to determine at what pressure explosive gaseous mixtures could be fired without injury to the apparatus. For passing the spark, a small Rühmkorff's coil worked with six Bunsen dichromate cells was used, or sometimes a smaller apparatus such as is sold commercially for igniting gas-flames (Clarke's Patent, Nos. 2229 and 245). The latter contains a dichromate cell, which is put in action by pressing a button, and can readily be adapted for firing the eudiometer by replacing the connectors by two flat brass springs. The eudiometer tube is placed between the two springs, and these are raised until they touch the loops of the platinum wires. On pressing the button, the spark passes. This only requires the use of *one* hand, and in conjunction with its portability, makes the apparatus very convenient. In this paper Rk. signifies the spark from the Rühmkorff, F. that from Clarke's machine.

Various hydrocarbons were mixed with somewhat more than the quantity of oxygen necessary for complete combustion, and the mixture tested as to its explosibility under greatly diminished pressure, which was gradually increased until the limit at which explosion took place was determined approximately. The numbers corresponding with the pressure at which explosion takes place are somewhat variable, as the size of the spark was not always the same. All the experiments were made with moist gases, that is, the eudiometer tube was wetted.*

1. *Methane*, CH_4.

The gas was prepared by heating a mixture of sodium acetate with soda-lime.

* In Thomas's memoir (*loc. cit.*), limits are given at which the explosion of mixtures of hydrogen and of some hydrocarbons with oxygen can take place without endangering the eudiometer tube. Thomas gives us convenient pressures:—

$H_2 + O$.....	200 mm.	pressure.
$CH_4 + 2{\cdot}5O_2$	170 „	„
$C_2H_6 + 4O_2$.....	120 „	„
$C_2H_4 + 3{\cdot}5O_2$	130 „	„
Heavy hydrocarbons.	130 „	„

He found the lowest limit for the explosion of $CH_4 + 2O_2$ to be 130 mm. pressure, whilst we have noticed explosion at 116·6 mm. Here the size of the spark, as might be imagined, greatly affects the result.

For complete combustion methane requires twice its volume of oxygen, as shown by the equation—

$$CH_4 + 2\,O_2 = CO_2 + 2H_2O.$$

The mixture contained 1 CH_4 to 2·297 oxygen.

Experiment.	Pressure in mm.	
I.	48·0, 63·0, 82·7, 106·1	Rk. no action.
	130·7	Rk. explosion.
II.	119·2	Ditto.
III.	114·4	Rk. no action.
„	122·0	„ explosion.
IV.	117·0	Ditto.
V.	116·6	Rk. explosion after several sparks.
VI.	140·0	F. explosion.
VII.	130·0	Ditto after several sparks.

For analysis, therefore, a pressure of 140 mm. should be used, as ignition will then take place even with a small spark.

2. *Propane*, C_3H_8.

The gas was prepared from propyl iodide and aluminium chloride according to Köhnlein's method (*Ber.*, **16**, 560).

Propane requires five times its volume of oxygen for combustion :—

$$C_3H_8 + 5\,O_2 = 3\,CO_2 + 4\,H_2O.$$

The mixture contained 5·645 volumes of oxygen to 1 of propane.

Experiment.	Pressure in mm.	
I.	41·4, 56·8	F., Rk. no action.
„	83·0	F. explosion.
II.	66·4	„ no action; Rk. explosion after several sparks.
III.	71·7	F. ditto.

With propane, explosion takes place quietly at a pressure of about 80 mm.

3. *Ethylene*, C_2H_4.

The gas was prepared by heating a mixture of alcohol with con-

centrated sulphuric acid. It requires three times its volume of oxygen :—

$$C_2H_4 + 3\,O_2 = 2\,CO_2 + 2\,H_2O.$$

The mixture contained 3·539 volumes of oxygen to 1 of ethylene.

Experiment.	Pressure in mm.	
I.	42·1	F. no explosion.
„	71·2	A moderate explosion.
II.	41·7 50·7	F. no action.
„	63·2	„ explosion after several sparks.
III.	35·6	Rk. immediate explosion.

When a feeble spark is used, ethylene requires a pressure of 70—80 mm. to insure explosion.

4. *Propylene*, C_3H_6.

The gas was prepared from thymol and phosphoric anhydride. It requires 4·5 times its volume of oxygen for complete combustion :—

$$C_3H_6 + 4{\cdot}5\,O_2 = 3\,CO_2 + 3\,H_2O.$$

The mixture contained 4·747 volumes of oxygen to 1 of propylene.

Experiment.	Pressure in mm.	
I.	31·6 37·6 50·3	F., Rk. no action.
„	89·3	F. explosion.
II.	53·7	F., Rk. no action.
„	64·5	F. explosion after several sparks.
III.	63·2	Ditto ditto.

A pressure of about 80 mm. is required.

5. *Acetylene*, C_2H_2.

The gas was separated from its copper compound by hydrochloric acid. It requires 2·5 times its volume of oxygen for combustion :—

$$C_2H_2 + 2{\cdot}5\,O_2 = 2\,CO_2 + H_2O.$$

The mixture contained 3·224 volumes of oxygen to 1 of acetylene.

Experiment.	Pressure in mm.	
I.	73·7	F. vigorous explosion.
II.	21·3 23·2	F., Rk. no action.

Experiment.	Pressure in mm.	
II.	32·4	F. moderate explosion.
III.	40·0	„ explosion.
„	28·2	F., Rk. no action.
„	32·7	F. good explosion.

A mixture of acetylene and oxygen, therefore, can be exploded without any danger under a pressure of 40—50 mm., whilst in Bunsen's eudiometer, even when a large proportion of nitrogen is present, the tube is often shattered (comp. E. v. Meyer, *J. pr. Chem.*, 1874, **10**, 323).

6. *Carbonic Oxide*, CO.

The gas was prepared from magnesium formate and sulphuric acid. It requires half its volume of oxygen for complete combustion :—

$$CO + \tfrac{1}{2}O_2 = CO_2.$$

The mixture contained 0·528 volume of oxygen to 1 of carbonic oxide.

Experiment.	Pressure in mm.	
I.	46·2 58·5 73·8 103·7 136·0 192·6	F., Rk. no action.
„	243·5	Good explosion.
II.	219·0	F. ditto.

A pressure of about 230 mm. should be used with a mixture of carbonic oxide with oxygen.

7. *Hydrogen*, H_2.

The mixture of oxygen with hydrogen was obtained by the electrolysis of water.

$$H_2 + \tfrac{1}{2}O_2 = H_2O.$$

Experiment.	Pressure in mm.	
I.	175·9	F. moderate explosion.
II.	143·0	„ feeble „
III.	54·0 60·0 72·7 85·0 101·0 115·0 124·2	F. no action.

Experiment.	Pressure in mm.	
III.	127·2	F. explosion after several sparks.
IV.	123·2	F. no action.
„	126·7	„ explosion after several sparks.
V.	125·0	Ditto ditto.
VI.	102·9	Rk. immediate explosion.
VII.	49·2	„ no action.
„	70·5	Kk. In this case, there was no action until several sparks had been passed, and even then there was no emission of light, and only part of the gas was burned; the remainder disappearing when the pressure was again increased to 72·2 mm. and the spark passed once more.

This observation was confirmed by two similar experiments.

Experiment.	Pressure in mm.	
VIII.	64·2	Rk. no action.
„	67·8	„ partial explosion as in VII.
„	72·1	„ the rest of the gas disappeared.
IX.	70·3	Rk. partial explosion.
„	72·9	„ the action completed.

On reading the volumes and pressures, and reducing them to 0° and 1000 mm., the following results were obtained:—

Experiment.	Burnt at first.	Residue burning when the pressure was increased.
VII.	73·16 per cent.	26·84 per cent.
VIII.	71·63 „	28·37 „
IX.	77·41 „	22·59 „

It would seem, therefore, that at a pressure of about 70 mm., but three-fourths of the gas is burnt, and the remainder only on increasing the pressure until it is the same as it was before the first explosion. This abnormal result is caused by the very high conductivity of hydrogen for heat, which cools the diluted gas so quickly, in spite of the high temperature produced by the combustion of the mixture, that at a distance from the source of heat the temperature sinks below that necessary to produce explosion. This is quite in accordance with the fact that when the explosion was effected by the small spark F, it was complete. The pressure in this case being more than 50 mm. greater, the gas was so dense that when ignition had once taken place the conductivity of the hydrogen was no longer able to extinguish it.

According to Bunsen (*Gasometrische Methoden*, 2nd Aufl., p. 338), the oxyhydrogen mixture no longer explodes if it is mixed with oxygen so that the percentage of the former is less than 9·66 (at 717 mm. pressure). This limit corresponds with a partial pressure of 70 mm. for the oxyhydrogen mixture, and, consequently, agrees with that found in our experiments. That the combustion in Bunsen's experiment was *complete*, whilst in ours it was only *partial*, shows that the expansion of a gas produced by diminishing the pressure is more effective in moderating the violence of explosion than when it is produced by diluting it with oxygen. As already noticed, Thomas had also made the same observation.

The combustion of the hydrocarbons and of carbonic oxide in presence of excess of oxygen was always complete, as after removal of carbonic anhydride by soda solution, the residual gas showed no diminution of volume on passing the spark, even when strongly compressed, and consisted merely of the excess of oxygen.

In these experiments, the gases burned under the following pressures:—

				Pressure in mm.
1 vol. methane with	about 2	vols.	oxygen..	116·6 Rk.
„	„ 2	„	..	130·0 F.
1 vol. propane	„ 5	„	..	66·4 Rk.
„	„ 5	„	..	71·7 F.
1 vol. ethane	„ 3	„	..	63·2 „
„ propylene	„ 4·5	„	..	63·2 „
„ acetylene	„ 2·5	„	..	32·4 „
„ carbonic oxide	„ 0·5	„	..	219·0 „
„ hydrogen	„ 0·5	„	..	125·0 „
„ „	„ 0·5	„	..	102·9 Rk.
„ „	„ 0·5	„	..	67·8—70·5 Rk. (only partially).

The order in which mixtures of these gases with the proper quantity of oxygen cease to ignite under diminished pressure is as follows:—First of all carbonic oxide, then methane and hydrogen, whilst propane, ethylene, and propylene are nearly equal, and acetylene comes last, and requires to be expanded to nearly double the extent of those immediately preceding it. The abnormal behaviour of oxyhydrogen mixture when greatly rarefied and with a strong spark has been already noticed.

Analyses.

When the limit of expansion at which the above gaseous mixtures could be safely exploded had been determined, a number of analyses were made of mixtures for which these furnished the material. Their

composition was only known incidentally, and they were determined both by the new and also by the old method (dilution with atmospheric air). The manner of carrying out these analyses is very simple. After the eudiometer has been completely filled with mercury in the usual manner, the gas to be analysed is introduced, so that the total volume of gas at the ordinary atmospheric pressure and after the addition of the necessary quantity of oxygen is only about one-tenth the capacity of the eudiometer. For example, in the apparatus employed, the width of the tube is 18 mm. and its area, therefore, 25 square cm., and a length of 400 mm. corresponds with 100 c.c.; about 10 c.c. of the explosive mixture is taken. With gases which do not require a very great diminution of the pressure, this limit may be proportionally exceeded.

In order to facilitate the measurement of these small volumes of gas, a small measuring vessel of about 2 c.c. is used for the air calibration of the eudiometer (Bunsen, *loc. cit.*, p. 74), and for analysis 1 vol. of the denser and 2 to 3 vols. of the lighter gases are taken.

As the amount of gas has to be determined from its volume and pressure, the measurements can be most accurately made if both the pressure and volume are represented by the same number of millimetres, as any inaccuracy in reading causes the error in the final result to be greater the smaller the absolute measurement, whether of pressure or volume. For example, if the possible error in the measurement of the pressure and volume is 0·1 mm. in 10 vols. measured at 500 mm. pressure, or in 500 vols. at 10 mm., it would be $\frac{0{\cdot}1}{10} + \frac{0{\cdot}1}{500} = 0{\cdot}0102$, or about 1 per cent., whilst if the same quantity of gas were measured at 70 vols. under a pressure of 71·43 mm., the error would be only $\frac{0{\cdot}1}{70} + \frac{0{\cdot}1}{71{\cdot}43} = 0{\cdot}0027$, or about a quarter per cent. In order to obtain this favourable result, it is merely necessary to place the reservoir Q at such a height that the surface of the mercury in B is nearly level with the upper closed end of the eudiometer E. The readings may be taken after the lapse of 15 to 20 minutes, as, with the small quantities of rarefied gas used, equilibrium is very soon established. The level of the mercury in the eudiometer and the corresponding number on the scale of the barometer are read first. If the axis of the cathetometer is accurately vertical, so that the telescope moves in a horizontal plane, the readings may be taken directly, but it is easier and sufficiently accurate if the distance between E and B is made so small that the scales of both are in the field at the same time. The graduations are illuminated by a white paper screen on E (Fig. 1, p. 582); by this means it is easy to read to 0·1 mm. The

height of the mercury surface in B and the temperature indicated by the thermometer *t* are read in the usual way.

The pressure is now diminished to the necessary extent, and the spark passed. If there is no explosion, Q is raised and the spark passed again. Explosion always takes place with a bright light, and so quietly that in spite of the small pressure-column of mercury, there is only a slight oscillation in E, and gas-bubbles are never forced down to the bottom of E. The sides of the eudiometer tube are washed by alternately lowering and raising Q, and the reading is taken after the pressure and volume of the residual gas have again been made as nearly equal as possible.

Soda solution of 7 per cent. NaHO, as recommended by Bunsen, is employed for absorbing the carbonic anhydride. The requisite quantity of it should be boiled in an Erlenmeyer's flask for about ten minutes to expel the absorbed air, and then introduced warm into the eudiometer. This is done by a pipette in the usual way after Q has been lowered so that the level of the mercury in the reservoir and trough is the same, and E has been disconnected. When the eudiometer is again in place, the pressure is increased so that the soda solution as nearly as possible reaches the spark-wires without actually wetting them. If this occurs, a slight error is caused by some of the liquid being retained between the wires and glass by capillary attraction, thus causing the volume of the gas to appear larger than it is. Correction for this minute error may be made, if the volume of the solution is read before increasing the pressure. With the small volume of gas, absorption of the carbonic anhydride proceeds very quickly, and may be considered as complete after the lapse of half an hour. The pressure and volume are then equalised as before, and a quarter of an hour later the readings are taken—of course observing the level of the soda solution also.

In calculating the analysis, the volumes corresponding with the divisions on the eudiometer are found from the calibration table, and a correction made for the meniscus. The pressure of the gas is the difference between the mercury level in B and E. A correction for the tension of water-vapour is not needed, as the barometer tube is wet. The only correction necessary is that required to reduce the pressure of the mercury as read on the glass scale to 0°, and this is very small, as the length is but short. In the absorption of the carbonic anhydride, the height of a column of mercury corresponding with the soda solution has to be deducted from the pressure, and the difference between the vapour-tension of soda solution and that of pure water to be added (Bunsen, *loc. cit.*, pp. 357 and 360).

We now give the analytical results exactly as recorded. It is however to be noted that the gases analysed were not quite pure, although

nearly so; any discrepancies in the analytical results, therefore, are not necessarily due to the methods employed.

For comparison, analyses of the same gaseous mixtures were made in Bunsen's eudiometer as well as in the apparatus described. As an example of the mode of working full details of the first analyses are given.

1. Methane and Oxygen.

$$\underset{3\text{ vol.}}{CH_4} + 2\,O_2 = \underset{1\text{ vol.}}{CO_2} + 2\,H_2O.$$

In these experiments p is the pressure in metres, b is the volume of combustible gas—

c, the contraction $= 2b$,
d, the carbonic anhydride $= 1b$.

Experiment I.

α. After introduction of the gaseous mixture—

Vol. read	179·0	Barometer level..	0·5930 m.
Vol. cor.	183·97	Level in E.....	0·3975 „
Temp. $t = 21·8°$			
		p =	0·1955
		p cor. =	0·19477

The pressure was diminished to 140 mm. and the spark passed.

β. After explosion—

Vol. read	110·5	Barometer level..	0·5237
Vol. cor.	116·38	Level in E.....	0·4030
$t = 21·9°$			
		p =	0·1207
		p cor. =	0·12025

Boiled solution of soda (7 per cent. NaHO) was introduced into the eudiometer.

γ. After absorption of the carbonic anhydride—

Mercury in E.....	48·0	Barometer level ...	0·4615
Vol. read	43·0	Level in E.....	0·3974
Vol. cor.....	48·69		
Soda solution.....	5·0	p =	0·0641
		p cor. =	0·06475

This calculated to 0° and 1000 mm. pressure gives—

Gas	33·184	Methane.
Difference c ...	20·233	$b = \frac{1}{2}c = 10·117$ or 30·49 per cent.
After explosion	12·951	
Difference d ...	10·033	$b = 1d = 10·033$ or 30·23 per cent.
After absorption		Difference 0·084
of CO_2	2·918	

Experiment II.

	Cor. vol.	Cor. pressure.	t.
Gas	147·3	0·16258	21·8°
After explosion	93·1	0·10053	21·8°
After absorption of CO_2.	40·9	0·05232	21·6°

Soda solution = 4·8.

This calculated to 0° and 1000 mm. pressure gives—

Gas	22·178	Methane.
Difference c....	13·510	$b = \frac{1}{2}c = 6·755$ or 30·46 per cent.
After explosion.	8·668	
Difference d ..	6·685	$b = 1d = 6·685$ or 30·14 per cent.
After absorption		Difference 0·070
of CO_2	1·983	

2. PROPANE AND OXYGEN.

$$\underset{\text{6 vol.}}{C_3H_8} + 5\,O_2 = \underset{\text{3 vol.}}{3\,CO_2} + 4\,H_2O.$$

In these experiments, b is the volume of combustible gas—
c, the contraction = $3b$,
d, the carbonic anhydride = $3b$.

Experiment I.

	Cor. vol.	Cor. pressure.	t.
Gas	149·3	0·15076	13·4°
After explosion	112·05	0·11125	13·5°
After absorption of CO_2..	48·1	0·04476	13·3°

Soda solution = 4·8.

This calculated to 0° and 1000 mm. pressure gives—

Gas	21·460	Propane.
Difference c....	9·582	$b = \frac{1}{3}c = 3·194$ or 14·88 per cent.
After explosion.	11·878	
Difference d....	9·825	$b = \frac{1}{3}c = 3·275$ or 15·26 per cent.
After absorption		Difference 0·081
of CO_2	2·053	

Experiment II.

	Cor. vol.	Cor. pressure.	t.
Gas	144·42	0·13622	12·2°
After explosion	101·07	0·10767	12·2°
After absorption of CO_2..	36·70	0·05206	12·4°

Soda solution = 4·0.

This calculated to 0° and 1000 mm. pressure gives—

Gas	18·832	Propane.
Difference c....	8·415	$b = \frac{1}{3}c = 2·805$ or 14·90 per cent.
After explosion.	10·417	
Difference d ..	8·589	$b = \frac{1}{3}d = 2·863$ or 15·20 per cent.
After absorption		Difference 0·058
of CO_2.....	1·828	

Experiment III.

	Cor. vol.	Cor. pressure.	t.
Gas	137·45	0·14907	12·8°
After explosion	105·33	0·10707	12·4°
After absorption of CO_2..	36·70	0·05402	12·0°

Soda solution = 6·0.

This calculated to 0° and 1000 mm. pressure gives—

Gas	19·574	Propane.
Difference c ..	8·786	$b = \frac{1}{3}c = 2·929$ or 14·96 per cent.
After explosion.	10·788	
Difference d ...	8·880	$b = \frac{1}{3}d = 2·960$ or 15·12 per cent.
After absorption		Difference 0·031
of CO_2.....	1·908	

Experiment IV (in Bunsen's Eudiometer).

In consequence of an accident, the mixture employed in the first three experiments could not be used for this, but in order to prove the purity of the propane a fresh mixture of propane and oxygen was prepared and analysed—

	Cor. vol.	Cor. pressure.	t.
Propane and O	187·27	0·31542	11·8°
After adding air.....	419·53	0·55060	11·2°
After explosion	382·66	0·51043	11·8°
After absorption of CO_2 .	337·72	0·47510	11·5°

Soda solution 7·6.

This calculated to 0° and 1000 mm. pressure gives—

Gas	56·624	
Gas and air....	221·900	Propane.
Difference c....	34·66	$b = \frac{1}{3}c = 11{\cdot}55$ or 20·4 per cent.
After explosion.	187·24	
Difference d...	33·81	$b = \frac{1}{3}d = 11{\cdot}27$ or 19·90 per cent.
After absorption of CO_2.....	153·43	Difference 0·28

3. Ethylene and Oxygen.

$$C_2H_4 + 3\,O_2 = 2\,CO_2 + 2H_2O.$$
4 vol. 2 vol.

In these experiments, b is the volume of combustible gas—
c, the contraction $= 2b$,
d, the carbonic anhydride $= 2b$.

The explosion was effected at about 100 mm. pressure.

Experiment I.

	Cor. vol.	Cor. pressure.	t.
Gas	66·06	0·41874	9·2°
After explosion	125·27	0·12545	9·0°
After absorption of CO_2..	69·03	0·04646	8·6°

Soda solution 3·8.

This calculated to 0° and 1000 mm. pressure gives—

Gas	26·761	Ethylene.
Difference c....	11·547	$b = \frac{1}{2}c = 5{\cdot}774$ or 21·58 per cent.
After explosion.	15·214	
Difference d...	12·105	$b = \frac{1}{2}d = 6{\cdot}053$ or 22·62 per cent.
After absorption of CO_2.....	3·109	Difference 0·279

Experiment II (in Bunsen's Eudiometer).

	Cor. vol.	Cor. pressure.	t.
Gas	303·9	0·28106	11·5°
Same with air	642·9	0·61905	11·3°
After explosion	612·6	0·58610	11·4°
After absorption of CO_2..	579·4	0·55321	11·7°

This calculated to 0° and 1000 mm. pressure gives—

Gas	82·418	
Gas and air....	381·96	Ethylene.
Difference c....	36·49	$b = \frac{1}{2}c = 18{\cdot}25$ or $22{\cdot}14$ per cent.
After explosion.	345·47	
Difference d....	35·90	$b = \frac{1}{3}d = 17{\cdot}95$ or $21{\cdot}78$ per cent.
After absorption		Difference 0·30
of CO_2.....	309·57	

4. Propylene and Oxygen.

$$C_3H_6 + 4{\cdot}5\ O_2 = 3\ CO_2 + 3\ H_2O.$$
$$5{\cdot}5 \text{ vol.} \qquad 3 \text{ vol.}$$

In these experiments, b is the volume of combustible gas—
c, the contraction $= 2{\cdot}5b$,
d, the carbonic anhydride $= 3b$.

The explosion took place under a pressure of 60 mm.

Experiment I.

	Cor. vol.	Cor. pressure.	t.
Gas	133·79	0·13039	9·8°
After explosion	101·95	0·10023	10·0°
After absorption of CO_2..	39·80	0·03165	10·2°

Soda solution = 4·1.

This calculated to 0° and 1000 mm. pressure gives—

Gas	16·833	Propylene.
Difference c....	6·975	$b = \frac{2}{5}c = 2{\cdot}790$ or $16{\cdot}57$ per cent.
After explosion.	9·858	
Difference d ...	8·644	$b = \frac{1}{3}d = 2{\cdot}881$ or $17{\cdot}12$ per cent.
After absorption		Difference 0·091
of CO_2.....	1·214	

Experiment II.

	Cor. vol.	Cor. pressure.	t.
Gas	131·42	0·13256	10·8°
After explosion	98·14	0·09852	10·7°
After absorption of CO_2..	26·28	0·02345	10·5°

Soda solution = 6·4.

This calculated to 0° and 1000 mm. pressure gives—

Gas	16·759	Propylene.
Difference c....	7·455	$b = \frac{2}{5}c = 2·982$ or 17·79 per cent.
After explosion.	9·304	
Difference d ...	8·711	$b = \frac{1}{3}d = 2·904$ or 17·33 per cent.
After absorption of CO_2	0·593*	Difference 0·078

Experiment III (in Bunsen's Eudiometer).

	Cor. vol.	Cor. pressure.	t.
Gas	277·29	0·23768	10·2°
Same with air.....	576·70	0·54442	9·8°
After explosion	552·91	0·51596	10·8°
After absorption of CO_2..	516·59	0·48671	11·8°

Soda solution = 6·2.

This calculated to 0° and 1000 mm. pressure gives—

Gas	63·534	
Gas and air....	303·100	Propylene.
Difference c....	28·66	$b = \frac{2}{5}c = 11·46$ or 18·04 per cent.
After explosion.	274·44	
Difference d ...	33·42	$b = \frac{1}{3}d = 11·14$ or 17·54 per cent.
Same after absorption of CO_2	241·02	Difference 0·32

5. Acetylene and Oxygen.

$$C_2H_2 + 2·5\ O_2 = 2\ CO_2 + H_2O.$$
$$3·5 \text{ vol.} \qquad 2 \text{ vol.}$$

In these experiments, b is the volume of combustible gas—
c, the contraction $= 1·5b$,
d, the carbonic anhydride $= 2·0b$.

The explosion took place under a pressure of 50 mm.

Experiment I.

	Cor. vol.	Cor. pressure.	t.
Gas	122·29	0·12770	8·8°
After explosion	104·52	0·09705	8·7°
After absorption of CO_2..	49·50	0·05479	8·5°

Soda solution = 3·9.

* This number is about 0·6 too small, as may be seen by comparison with Experiment I. That a larger volume of oxygen was used is due to the fact that it went to oxidise a small quantity of mercury adhering to the wires of the eudiometer. If this 0·6 be subtracted from the contraction c, this becomes 6·855, and the propylene 2·742 or 16·36 per cent.

This calculated to 0° and 1000 mm. pressure gives—

Gas	15·129	Acetylene.
Difference c....	5·298	$b = \frac{3}{5}c = 3·532$ or 23·35 per cent.
After explosion.	9·831	
Difference d....	7·201	$b = \frac{1}{2}d = 3·601$ or 23·80 per cent.
After absorption of CO_2	2·630	Difference 0·069

Experiment II.

	Cor. vol.	Cor. pressure.	t.
Gas	124·57	0·11502	8·7°
After explosion	104·14	0·08956	8·7°
After absorption of CO_2..	52·60	0·04678	8·9°

Soda solution = 3·7.

This calculated to 0° and 1000 mm. pressure gives—

Gas	13·886	Acetylene.
Difference c....	4·847	$b = \frac{3}{5}c = 3·231$ or 23·27 per cent.
After explosion.	9·039	
Difference d ..	6·656	$b = \frac{1}{2}d = 3·328$ or 23·97 per cent.
After absorption of CO_2.....	2·383	Difference 0·097

Experiment III (in Bunsen's Eudiometer).

	Cor. vol.	Cor. pressure.	t.
Gas	248·9	0·21432	9·1°
Same with air.....	554·12	0·52264	9·4°
After explosion	537·0	0·50500	9·2°
After absorption of CO_2..	510·26	0·48112	9·4°

Soda solution = 6·5.

This calculated to 0° and 1000 mm. pressure gives—

Gas	51·625	
Gas and air....	279·973	Acetylene.
Difference c....	17·620	$b = \frac{3}{5}c = 11·747$ or 22·75 per cent.
After explosion.	262·353	
Difference d...	25·022	$b = \frac{1}{2}d = 12·511$ or 24·23 per cent.
After absorption of CO_2.....	237·331	Difference 0·764

In conclusion, we give the analyses of some of the gases carried out in the manner described.

Analyses of Methane.

Analysis I.	Cor. vol.	Cor. pressure.	*t.*
Oxygen	187·84	0·20114	22·3°
After adding methane ..	209·65	0·22086	22·3°
After explosion.....	167·53	0·17363	22·3°
After absorption of CO_2..	134·81	0·15461	22·3°

Soda solution = 4·9.

Explosion took place under a pressure of 160 mm. Calculated to 0° and 1000 mm. pressure it gives—

Oxygen.....	34·931		Methane.
Difference *b* ...	7·879	b =	7·879
After adding methane	42·810		
Difference *c*....	15·917	$b = \frac{1}{2}c$ =	7·959
After explosion.	26·893		
Difference *d* ...	7·623	$b = 1d$ =	7·623
After absorption of CO_2.....	19·270	Difference	0·336

Analysis II.	Cor. vol.	Cor. pressure.	*t.*
Oxygen	162·81	0·17440	22·0°
After adding methane...	191·22	0·20895	22·1°
After explosion	122·79	0·13828	21·8°
After absorption of CO_2..	69·47	0·08286	21·7°

Soda solution = 5·6.

This calculated to 0° and 1000 mm. pressure gives—

Oxygen.....	26·278		Methane.
Difference *b*....	10·687	b =	10·687
After adding methane	36·965		
Difference *c*....	21·240	$b = \frac{1}{2}c$ =	10·620
After explosion.	15·725		
Difference *d*....	10·391	$b = 1d$ =	10·391
After absorption of CO_2.....	5·334	Difference	0·229

Analysis of Propane.

	Cor. vol.	Cor. pressure.	*t.*
Oxygen	185·36	0·21010	19·4°
After adding propane...	210·9	0·21838	19·2°
After explosion	150·8	0·16068	18·9°
After absorption of CO_2..	41·4	0·04930	18·8°

This calculated to 0° and 1000 mm. pressure gives—

Oxygen.....	36·362		Propane.
Difference b....	6·669	$b =$	6·669
After adding propane.....	43·031		
Difference c....	20·369	$b = \frac{1}{3}c =$	6·790
After explosion.	22·662		
Difference d....	20·752	$b = \frac{1}{3}d =$	6·917
After absorption of CO_2.....	1·910	Difference	0·127

Analysis of Acetylene.

	Cor. vol.	Cor. pressure.	t.
Oxygen	126·46	0·12750	18·0°
After adding acetylene..	136·78	0·14665	18·0°
After explosion	113·82	0·12491	18·0°
After absorption of CO_2..	67·54	0·08857	18·4°

This calculated to 0° and 1000 mm. pressure gives—

Oxygen.....	15·127		
Difference b....	3·692	$b =$	3·692
After adding acetylene....	18·819		
Difference c....	5·480	$b = \frac{3}{5}c =$	3·653
After explosion.	13·339		
Difference d...	7·734	$b = \frac{1}{2}d =$	3·867
After absorption of CO_2.....	5·605	Difference	0·214

TABLE OF ANALYTICAL RESULTS.

I. *Mixture of Gases with Oxygen.*

B signifies that the analysis was made in a Bunsen's eudiometer; α gives the percentage calculated from the contraction, β that from the carbonic anhydride formed, and γ the differences between these two.

	α.	β.	γ.
Methane—			
Experiment I	30·49	30·23	− 0·26
„ II	30·46	30·14	− 0·32
Propane—			
Experiment I	14·88	15·25	+ 0·38
„ II	14·90	15·20	+ 0·30
„ III	14·96	15·12	+ 0·16
„ IV (B)	[20·40	19·90	− 0·50]
Ethylene—			
Experiment I	21·58	22·62	+ 1·04
„ II (B)	22·14	21·78	− 0·36
Propylene—			
Experiment I	16·57	17·12	+ 0·55
„ II	17·79	17·33	− 0·46
„ III (B)	18·04	17·54	− 0·50
Acetylene—			
Experiment I.....	23·35	23·80	+ 0·45
„ II	23·27	23·97	+ 0·70
„ III (B)	22·75	24·23	+ 1·48

II. *Combustible Gas Measured by Itself.*

The measurements are corrected to 0° and 1000 mm. A is the volume taken; α that calculated from the contraction, β that from the carbonic anhydride formed, and γ the difference.

	A.	α.	β.	γ.
Methane—				
Analysis I.....	7·879	7·959	7·623	0·336
„ II.....	10·687	10·620	10·391	0·229
Propane	6·669	6·790	6·917	0·127
Acetylene.....	3·692	3·653	3·867	0·214

A comparison of the results given in these tables shows that the diminished pressure method gives results quite as favourable as those obtained by dilution with nitrogen or atmospheric air, moreover, it has the advantages of being more rapid and of avoiding the inconvenience arising from either too violent or incomplete explosion, which may occur when nitrogen is used.

Our apparatus requires very careful work on the part of the maker

so that the iron plug may fit perfectly air-tight into the base of the trough. After some preliminary trials, however, it was found that this delicate and somewhat costly contrivance could be replaced by a simpler one; the modified apparatus is represented in Fig. 3 (p. 582). In this both the eudiometer and the barometer are connected with the glass tube *g*, by good vulcanised india-rubber corks, the broad ends of which are let into the bottom of the trough, and if necessary are cemented to it. In this way a perfectly tight joint is formed under the mercury. The tube *g* should be somewhat longer than the barometric column, so that there may be no danger of air entering where it is connected with the covered tube at its lower end. If this should happen, it can only enter the barometer tube, from which it may readily be removed by raising Q. In this method of fastening the tubes, it is necessary to support them, which may be most conveniently effected by using a stand similar to that employed with Bunsen's trough. If the reservoir is globular, the table and supports need not be so high, or the reservoir may be used with a detached support (W. Hempel, *loc. cit.*, p. 93, Fig. 14).

We intend to improve and extend this method as far as possible. The saving of time is a great advantage, as an analysis can be completed in three to four hours, and the difficulty arising, even in skilled hands, from too violent or incomplete combustion when air is used is avoided. Moreover, the manipulation of the apparatus is simple, and the results obtained even with small quantities of gas are sufficiently accurate.

XLIX.—*Calculation of Gas Analyses.*

By Lothar Meyer.

In reference to the previous paper I may add some remarks on the advantages of adhering strictly to Avogadro's law on the calculation of gas analyses. Although previous to the publication of *Bunsen's Gasometry*, Avogadro's law was neither in general use nor even recognised, yet every analytical process of this kind depended either on this rule or on the property discovered by Gay-Lussac, that all gases combine or react in simple volume-proportions.

The principles of the mode of calculation have been long established, but the manner of doing this may be simplified by employing the now generally used volume formulæ. If we write all formulæ so that they represent the molecular weights according to Avogadro's

law—that is, the weights which in the gaseous state occupy equal volumes at the same temperature and under the same pressure, the equation representing the decomposition will at once give the change in volume which accompanies the decomposition and which serves for the calculation of the composition of the analysed gases.

As all hydrocarbons contain an even number of hydrogen-atoms in the molecule, an expression of the form C_nH_{2m}, in which n and m are whole numbers, may be made to represent the composition of any hydrocarbon. The possible values of m and n are only limited by the rule that m cannot be greater than $n + 1$, but may be less; in other respects as far as our present knowledge extends, m and n may have any other conceivable value. As, however, the volatility of hydrocarbons decreases as the molecular weight increases, m and n are always small numbers in the compounds which come within the scope of gas analysis.

The complete combustion of a hydrocarbon, C_nH_{2m}, by means of oxygen, takes place in accordance with the equation—

$$C_nH_{2m} + \left(n + \frac{m}{2}\right)O_2 = nCO_2 + mH_2O,$$

for $2n$ atoms or n mols. of oxygen are required to burn n carbon-atoms, and m atoms or $\frac{m}{2}$ mols. of oxygen for $2m$ hydrogen-atoms. During combustion, n mols. carbonic anhydride and m mols. of water are formed. Now as equal molecular weights of gases occupy equal spaces, the number of volumes of carbonic anhydride yielded by one volume of the combustible gas—both being at the same temperature and under the same pressure—gives at once the number, n, of carbon-atoms in a molecular weight of the hydrocarbon; whilst the number m, corresponding with the volume of water-vapour produced, is half the number of hydrogen-atoms contained in a molecular weight of the combustible gas. But although the carbonic anhydride produced may be directly determined by absorption with potash or soda, the amount of water-vapour produced can only be measured above its boiling point. As this is somewhat inconvenient, and, moreover, the operation can only be carried out with perfectly dry gases, the water is generally estimated in the manner suggested by Bunsen from the contraction produced by the disappearance of that portion of the oxygen which has combined with the hydrogen of the combustible gas to produce water; that which has served for the oxidation of the carbon having yielded an equal volume of carbonic anhydride. If we suppose—as in all these calculations—that the volumes are measured at the same temperature and under the same pressure, we find that a contraction—

$$c = b\left(1 + \frac{m}{2}\right),$$

takes place in the combustion of the volumes of the hydrocarbon C_nH_{2m}, whilst the carbonic anhydride $d = nb$. From this it follows that—

$$n = \frac{d}{b} \text{ and } m = 2\,\frac{c - b}{b}.$$

By the use of these fundamental equations, we can at once calculate the composition of the gas from the contraction c and the carbonic anhydride d.

If the gas is homogeneous, n and m will come out as whole numbers, for example, Bunsen (*Gasom. Method.*, 2 Aufl., p. 213) found for a gas collected from a mud volcano at Bulganak in the Crimea—

$$b = 20{\cdot}01 \quad c = 41{\cdot}18 \quad d = 20{\cdot}32;$$

and from this—

$$n = \frac{20{\cdot}32}{20{\cdot}01} = 1{\cdot}01 \quad m = \frac{2(41{\cdot}18 - 20{\cdot}01)}{20{\cdot}01} = 2{\cdot}11.$$

Allowing for unavoidable errors of observation, the composition of the gas was $C_nH_{2m} = CH_4$; that is, pure methane or marsh-gas.

If n and m do not come out as whole numbers, it necessarily follows that *the gas is a mixture*, although, on the other hand, whole numbers may also correspond with a gaseous mixture if the components are in a certain ratio dependent on the nature of the gases (Bunsen, *loc. cit.*, p. 300). The class to which the analysed gas belongs is easily ascertained from the laws governing the molecular composition.

For Paraffins or gases of the marsh-gas series, C_nH_{2n+2}, the first member has $n = 0$, that is, $C_0H_2 = H_2$, or hydrogen

$$m = n + 1 \qquad m - n = 1,$$

or, taking the values from the fundamental equation—

$$\frac{2(c - b) - d}{b} = 1, \text{ or } \frac{2(c - b)}{b} = 3.$$

This is the maximum difference possible for $m - n$, as no hydrocarbon is known containing more than $2(n + 1)$H to nC. In the analysis above quoted, therefore, where $n = 1{\cdot}01$, $m = 2{\cdot}11$, $m - n = 1{\cdot}10$.

The slight excess in the value of m can only be due to errors of observation (the observed contraction being somewhat too high), and not to impurity in the gas, as there is no gas which would make the value $m - n > 1$ when mixed with methane.

For the Olefines or gases of the ethylene series, C_nH_{2n},

$$m = n \qquad m - n = 0$$

$$\frac{2(c-b)-d}{b} = 0, \text{ or } \frac{2(c-b)}{b} = 2.$$

For Acetylene and its homologues, C_nH_{2n-2},

$$m = n - 1 \qquad m - n = -1$$
$$\frac{2(c-b)-d}{b} = -1, \text{ or } \frac{2(c-b)}{b} = 1.$$

For the Valylene series and the vapour of Oil of Turpentine, C_nH_{2n-4},

$$m = n - 2 \qquad m - n = -2$$
$$\frac{2(c-b)-d}{b} = -2 \text{ or } \frac{2(c-b)}{b} = 0.$$

Finally, for Benzene vapour and that of its homologues C_nH_{2n-6},

$$m = n - 3 \qquad m - n = -3$$
$$\frac{2(c-b)-d}{b} = -3 \quad \frac{2(c-b)}{b} = -1.$$

These rules hold good not only for simple gases but also for mixtures, provided always that all the constituents of the mixture belong to one and the same class of compounds.

Suppose it is found that $b = 1$, $d = 2{\cdot}6$, and $c = 2{\cdot}8$, then—

$$n = 2{\cdot}6, \; m = 2(2{\cdot}8 - 1) = 3{\cdot}6, \text{ and } m - n = 1,$$

we have a mixture of paraffins which in the unit of volume contains 0·6 C more than ethane. This corresponds with a mixture of 0·6 vol. propane and $(1 - 0{\cdot}6) = 0{\cdot}4$ vol. ethane :—

	n.	m.
0·4 C_2H_6.....	$0{\cdot}4 \times 2 = 0{\cdot}8$	$0{\cdot}4 \times 3 = 1{\cdot}2$
0·6 C_3H_8.....	$0{\cdot}6 \times 3 = 1{\cdot}8$	$0{\cdot}6 \times 4 = 2{\cdot}4$
	together $n = 2{\cdot}6$	$m = 3{\cdot}6$

	d.	c.
0·4 C_2H_6.....	$0{\cdot}4 \times 2 = 0{\cdot}8$	$0{\cdot}4 \times 2{\cdot}5 = 1{\cdot}0$
0·6 C_3H_8.....	$0{\cdot}6 \times 3 = 1{\cdot}8$	$0{\cdot}6 \times 3 = 1{\cdot}8$
	together $d = 2{\cdot}6$	$c = 2{\cdot}8$

In spite of the close agreement of the calculation with the results, this is only one of very many possible solutions of the problem. For example, we may have—

	n.	m.
0·4 C_4H_{10}	$0·4 \times 4 = 1·6$	$0·4 \times 5 = 2·0$
0·2 C_3H_8.....	$0·2 \times 3 = 0·6$	$0·2 \times 4 = 0·8$
0·1 C_2H_6.....	$0·1 \times 2 = 0·2$	$0·1 \times 3 = 0·3$
0·2 CH_4.....	$0·2 \times 1 = 0·2$	$0·2 \times 2 = 0·4$
0·1 H_2.....	$0·1 \times 0 = 0·0$	$0·1 \times 1 = 0·1$
	together $n = 2·6$	$m = 3·6$

In fact, the conditions are fulfilled by any mixture of paraffins—

$$xC_nH_{2n+2} + yC_{n'}H_{2n'+2} + zC_{n''}H_{2n''+2} + \ldots . \text{ \&c.},$$
$$\text{where } x + y + z + \ldots . \text{ \&c.} = b,$$
$$nx + n'y + n''z + \ldots . \text{ \&c.} = d,$$

the coefficients n, n', n'', &c., being whole numbers. We have here only two equations to determine an indefinite number of unknowns; for the contraction does not give a third equation, as it has already been used to show that the mixture contains nothing but paraffins.

The problem, therefore, cannot be solved, as may be seen, moreover, from the following considerations:—A molecular weight of any paraffin, C_nH_{2n+2}, occupies the same volume as H_2; also that of the excess of hydrogen in the paraffin over and above $n(CH_2)$. Now, suppose any given space filled with hydrogen, and let us combine p times $n(CH_2)$ with the p mols. hydrogen contained therein $= pH_2$, then it is evident that as far as the analytical results are concerned, it is indifferent whether we combine each of the p molecules of hydrogen, H_2, with $n(CH_2)$, or the half of them with $2n(CH_2)$, or the third with $3n(CH_2)$, or generally $\frac{1}{q}$ of them with $q \,.\, n(CH_2)$. A graphic representation of this will make the matter more evident. If each square represents a molecular volume, we may, for example, have the following mixtures, all of which will give the same analytical results as marsh-gas:—

CH_4	CH_4	CH_4	CH_4

H_2	H_2	C_2H_6	C_2H_6

H_2	CH_4	CH_4	C_2H_6

H_2	H_2	H_2	C_4H_{10}

and similarly for other paraffins.

By eudiometric analysis, it is possible to ascertain whether a gas is a paraffin; but we cannot with certainty decide as to which of these it is.

Strictly speaking, therefore, the analytical results always admit of many interpretations, as Bunsen has emphatically stated (*loc. cit.*, p. 300). In practice, this uncertainty is not of much moment. If the analysis gives m and n as whole numbers, generally there will be no hesitation in affirming the presence of a homogeneous compound, such as a hydrocarbon, C_nH_{2n+4}. With fractional values of n, one will naturally take the nearest whole numbers; for instance if $n = 2{\cdot}5$, then a mixture of C_2H_6 and C_3H_8 in equal volumes, &c. Generally the reactions in which the gas has been obtained will give some indication. For example, if a gas has been formed from ethyl, C_2H_5, and hydrogen, ethane might be expected; but analysis will not determine whether this has been produced, or a mixture of equal volumes of tetrane, (diethyl), C_4H_{10}, and hydrogen. In such cases, other means must be resorted to, such as the alteration in the composition of the mixture by diffusion (Bunsen, *loc. cit.* p. 301), absorption by liquids (*ibid.*, p. 249), condensation of the more volatile portions, action of chlorine in daylight, and separation of the chlorides by fractional distillation (Schorlemmer, *Annalen*, **131**, 76, and **132**, 234), &c. If the mixture contains hydrogen, the method of oxidation by means of palladium may be employed (Hempel, *Neue Method. z. Anal. der Gase*, 1880, p. 71).

A like uncertainty attends the analysis of the olefines and members of other series; as however the first members of the series C_nH_{2n} and C_nH_{2n-2} both contain two atoms of carbon, there can be no doubt as to the presence of pure ethylene or pure acetylene, when $n = 2$ and $m = 2$ or 1 respectively. It is quite evident, however, that if we suppose the whole space to be filled with C_2H_4 or C_2H_2 respectively, any excess of CH_2 found may be apportioned to the single molecules of gas in various ways, so that whenever $n > 2$, the analytical results may be produced by different mixtures.

If the combustible gas to be analysed is mixed with free oxygen or with carbonic anhydride, &c., these must of course be removed by appropriate absorbents before explosion. Such admixtures therefore need not be considered here. If, however, it contains nitrogen, which cannot be removed by these means, the volume b of the combustible constituent is unknown, and other means are required to determine the composition of the gas. In Bunsen's method, the new factor is the contraction, c', which takes place on the combustion with hydrogen of the excess of oxygen remaining after the first explosion, and absorption of the carbonic anhydride. A third of this second contraction, $\frac{1}{3}c'$, is due to oxygen, two-thirds, $\frac{2}{3}c'$, to that of the added hydrogen. We can calculate the required number from these results in two ways. If we subtract the hydrogen consumed from the total quantity added, the remainder is the unburned residue of this gas,

and the excess over this remaining after the second explosion is nitrogen. If air has been added, we must subtract from this the nitrogen in the added air. If there be any remainder, this will be the volume of nitrogen n originally present in the gas a, and we have

$$b = a - \mathrm{N},$$

which is the value to be employed in the fundamental equations.

Again if we subtract $\frac{1}{3}c'$ from the oxygen added, the remainder is the oxygen, o, consumed in the first explosion, of which d volumes were employed in the formation of carbonic anhydride, and the rest for the oxidation of the hydrogen. The latter portion together with the combustible gas make up the first contraction c. We have therefore—

$$o - d = \frac{m}{2} b \qquad b = c - (o - d),$$

$$\text{and } n = \frac{d}{b} = \frac{d}{c - o + d} \qquad m = \frac{2(o - d)}{c - o + d}.$$

The results obtained by the two modes of calculation are of course identical.

As an example, we will take the analysis of a gas from a pond in the Botanical Gardens at Marburg after it had been freed from carbonic anhydride (Bunsen, *loc. cit.*, p. 128).

A	35·47		
Air added	82·41	=	65·14 N 17·27 O
Oxygen added	29·04	Total O =	46·31
First contraction, c	34·38	Residual O	11·89
Carbonic anhydride, d..	17·28	o =	34·42
Hydrogen added	61·81		
Second contraction, c' ..	35·66	=	11·89 O 23·77 H
Residue	121·41		38·04 residual H.
Subtract residual H ...	38·04		
Nitrogen	83·37		
Subtract added N	65·14		
N =	18·23		
$b = a - \mathrm{N}$ =	17·24		

$$n = \frac{d}{b} = \frac{17{\cdot}28}{17{\cdot}24} = 1{\cdot}00 \quad m = \frac{2(c - b)}{b} = 2 \times \frac{34{\cdot}38 - 17{\cdot}24}{17{\cdot}28} = 1{\cdot}99,$$

$$\text{or } m = \frac{2(o - d)}{c - (o - d)} = 2 \times \frac{34{\cdot}42 - 17{\cdot}28}{34{\cdot}38 - 17{\cdot}14} = 1{\cdot}99 \quad m - n = 0{\cdot}99.$$

The gas therefore is a paraffin, methane, mixed with free nitrogen.

If there is no admixture of nitrogen with the combustible gas, the second explosion may be omitted, as it is all one whether the absorbed oxygen serving for the calculation of m is determined from the contraction produced by the first explosion or by the second; the latter, however, may be used as a control.

If the gas to be analysed contains any combined oxygen, this also goes into the products of combustion, the formation of which requires so much the less oxygen the more there is in the compound. The contraction is thereby diminished to the extent of one half volume O_2 for each atom of oxygen in a molecular weight of the compounds. The use of the fundamental formulæ—

$$n = \frac{d}{b}, \qquad m = \frac{2(c-b)}{b},$$

would in this case give the correct amount of carbon, but too little hydrogen in the proportion of H_2 for each atom of oxygen in a molecular weight of the compounds. For instance, whilst a hydrocarbon, C_mH_{2m}, gives a contraction of $c = 1 + \frac{m}{2}$, for each volume, a compound $C_mH_{2m}O_p$ will give a contraction $c = 1 + \frac{m}{2} - \frac{p}{2}$.

An oxygen compound of this kind behaves like a hydrocarbon, $C_nH_{2(m-p)}$ *containing* $2p$ *less hydrogen, or as if its oxygen, before explosion, were already combined with part of the hydrogen to form water.*

In order to distinguish oxygen compounds from the corresponding hydrocarbons, it is necessary to measure the water produced by the combustion of the carefully dried gas as water-vapour (Bunsen, *loc. cit.*, 54). For example, in the analysis of methyl oxide (*ibid.*, p. 57),

$$b = 24{\cdot}63 \qquad c = 50{\cdot}68 \qquad d = 49{\cdot}28,$$

$$n = \frac{d}{b} = 2{\cdot}00 \qquad m = \frac{2(c-b)}{b} = 2{\cdot}11.$$

The gas therefore might have been mistaken for ethylene, C_2H_4, if the measurement at 99·5° had not shown that it had given three times and not twice its volume of water-vapour. This observation rendered it possible to give the correct equation representing the oxidation. The free oxygen used is $O = c - b + d = 75{\cdot}53$, or for 1 vol. of the gas, $\frac{o}{b} = \frac{75{\cdot}33}{24{\cdot}63} = 3{\cdot}06$. If now we put x for the unknown molecular weight, the equation representing the combustion becomes—

$$x + 3O_2 = 2CO_2 + 3H_2O,$$

$$\text{and } x = 2C + 6H + 7O - 6O = C_2H_6O.$$

The two equations—

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O,$$
$$C_2H_6O + 3O_2 = 2CO_2 + 3H_2O,$$

for ethylene and methyl oxide respectively, show that in the analysis the latter burns like a hydrate of ethylene, C_2H_4,H_2O. Other oxygen compounds behave in an analogous manner.

If the gas contains no combined oxygen, the measurement of the water-vapour serves at most as a control, and is not absolutely necessary, as the water formed during combustion is more accurately and readily measured by the contraction. Measurement of the water-vapour is also superfluous for oxygen compounds about which no mistake can arise, as when there is no corresponding hydrocarbon, or when this can be readily recognised.

Methyl alcohol, $CH_4O = CH_2,H_2O$, could only be mistaken for the unknown hydrocarbon *methylene*, CH_2, or for a mixture of acetylene, C_2H_2, with hydrogen in equal volumes, which can be easily separated.

Methylene oxide or Formaldehyde, CH_2O, is oxidised in accordance with the equation—

$$CH_2O + O_2 = CO_2 + H_2O;$$

here $d = b$, and $c = b$,

$$m = \frac{d}{b} = 1 \quad m = \frac{2(c-b)}{b} = 0 \quad m - n = 1.$$

Formaldehyde therefore, on analysis, behaves like a hydrocarbon of the acetylene series of the formula CH_0, or as carbon vapour. There is no gas for which this can be mistaken, so that $n = 1$ and $m = 0$ are characteristic of formaldehyde, &c.

Carbonic oxide requires special consideration. The combustion equation is—

$$CO + \tfrac{1}{2}O_2 = CO_2.$$
$$d = b \qquad c = \tfrac{1}{2}b.$$

Substituting these values in the fundamental equations we have—

$$n = \frac{d}{b} = 1 \quad m = \frac{2(c-b)}{b} = -1 \quad m - n = -2.$$

The negative value of m signifies that the carbonic oxide contains two atoms of hydrogen less than would be sufficient to combine with its oxygen. As carbonic oxide is the only gas* which gives a negative

* Carbon oxysulphide, COS, when exploded in a moist state, gives $c = 1{\cdot}5$, but if dry $c = 0{\cdot}5$. If dry, it might be mistaken for CO, but is removed by the preliminary treatment with potash.

value for m, its presence is certain if $m < 0$; and if methylene oxide is known to be absent, we may be sure that carbonic oxide is present if $m < 1$; as we know of no hydrocarbon containing less than two hydrogen atoms in a molecular weight.

As an example, I give Long's analysis of the gases formed by passing water-vapour over red-hot charcoal (*Annalen*, **192**, 290). Analysis No. 3 gave—

a	114·24	=	100·00 per cent.
$- CO_2$	83·57		73·16 „
	30·67		26·84

from the residue after explosion—

$$b = 46{\cdot}22$$
$$c = 61{\cdot}01$$
$$d = 8{\cdot}34$$

$$n = \frac{d}{b} = 0{\cdot}180 \quad m = \frac{2(c-b)}{b} = 0{\cdot}640.$$

As $m < 1$, and from the manner in which the gas was formed formaldehyde could scarcely be present, carbonic oxide is to be expected, the proportion of which can be calculated from the value of $n = 0{\cdot}180$. Its presence makes the hydrogen present in the other constituent appear too low. In order to find the value of m for the residual 0·820 vol. reckoned on the unit value, we must subtract that corresponding with the CO found $= -0{\cdot}180$ volume—

$$0{\cdot}820\, m = 0{\cdot}640 - (-0{\cdot}180) = 0{\cdot}820$$
$$m = 1 \qquad 2m = 2$$

The gas is consequently H_2, that is, hydrogen. The percentages of the gases present are—

Carbonic oxide..	$0{\cdot}180 \times 73{\cdot}16 = 13{\cdot}17$
Hydrogen.....	$0{\cdot}820 \times 73{\cdot}16 = 59\ 99$

In order to calculate the composition of any mixture of gases which contains $xC_{n_1}H_{2m_1} + yC_{n_2}H_{2m_2} + zC_{n_3}H_{2m_3} + \ldots$ &c., in a unit of volume and when n and m have the value calculated from the analysis—

$$n = xn_1 + yn_2 + zn_3 + \ldots \text{ &c.}$$
$$m = xm_1 + ym_2 + zm_3 + \ldots \text{ &c.}$$
$$1 = x + y + z + \ldots \text{ &c.}$$

Here both the quantities x, y, z, &c., of the gas contained in the unit of volume are unknown, and also the coefficients n_1, n_2, n_3, &c.

and m_1, m_2, m_3, &c., expressing the composition of the individual gases. For their determination, however, we have besides the three equations given above, the conditions that x, y, z, &c., must always be *positive fractional* numbers, n_1, n_2, n_3, &c., and m_1, m_2, m_3, &c., *positive whole* numbers, and that m_1 cannot be greater than $n_1 + 1$, m_2 greater than $n_2 + 1$, &c. So long, however, as we are unable to express these conditions in the form of equations, we can merely endeavour to assign such arbitrary values to n_1, n_2, &c., and m_1, m_2, &c., as will give positive values for x, y, z, &c. When there is no special reason to suspect the presence of any particular compounds, the whole numbers nearest to the values found for m and n should be tried first.

A gaseous mixture obtained by the action of alcoholic potash on bromoform (Hermann, *Annalen*, **95**, 214; Long, *ibid.*, **194**, 25), gave—

$$b = 21{\cdot}76 \quad c = 18{\cdot}88 \quad d = 27{\cdot}12$$

$$n = \frac{d}{b} = 1{\cdot}247 \quad m = \frac{2(c-b)}{b} = -0{\cdot}265 \quad m - n = -1{\cdot}512.$$

As the value of n lies between the whole numbers 1 and 2, the simplest assumption is that the mixture consists of two gases of which one contains C and the other C_2 in the molecular weight, and that $n_1 = 1$ and $n_2 = 2$. That the first gas must be carbonic oxide follows from the calculated difference between m and n—

$$\begin{aligned} x + \ \ y &= 1 \\ x + 2y &= n = 1{\cdot}247 \\ -x + ym_2 &= m = -0{\cdot}265, \end{aligned}$$

from which we find—

$$x = 0{\cdot}753, \qquad y = 0{\cdot}247 \qquad m_2 = 1{\cdot}977.$$

As we have obtained for m a value differing but little from a whole number, we can make $m_2 = 2$. The analysis shows that the gas is a mixture of three parts carbonic oxide with one part of ethylene.

If on the other hand we make $n_2 = 3$, we shall find that—

$$x = 0{\cdot}8765 \quad y = 0{\cdot}1235, \text{ and } m_2 = 4{\cdot}952.$$

This corresponds with a hydrocarbon of the formula C_3H_{10}: as however no such compounds exist, it is evident that $n_2 = 3$ is inadmissible. It is unnecessary to give other examples.

Although the method of calculation just given often leaves us in doubt as to the composition of a gaseous mixture, yet a systematic manner of calculation like this has many advantages over the more desultory one usually employed.

L.—*Note on the Chemical Alterations of Green Fodder during its Conversion into Ensilage.*

By Dr. O. Kellner, Imperial College of Agriculture, Tokio.

In a short preliminary contribution to the chemistry of ensilage, Professor Edward Kinch recently recorded the results of a few analyses of grass and of the ensilage made therefrom, introducing the account of his experiments in the following words:—"Whether, during the fermentations to which grass and other fodder crops are subjected in order to produce ensilage, the albuminoïds which they contain undergo any change into other nitrogenous bodies not having the physiological functions of albuminoïds, and to what extent such changes occur, is a matter not only of much scientific interest, but of great practical importance in considering the economic relations of ensilage. This point has been hitherto unnoticed in published analyses of ensilage, although it seems very likely such changes would occur during the processes, in some respects allied to digestion, to which the fodder is subjected" (*Chem. Soc. J.*, this vol., 123).

Mr. Warington, commenting on these researches, said: "As far as he knew, Professor Kinch had been the first to determine the relative quantities of albuminoïd and non-albuminoïd nitrogen in ensilage. There had been many analyses of grass and ensilage published, but no one yet had really made a quantitative experiment, *i.e.*, weighed all the grass which went in and the ensilage produced" (*Chem. News*, February 15th, 1884, 78).

The subject in question really deserves great attention, as at the present time American and French farmers are so enthusiastic about the preparation of ensilage, practised since remote times in Germany: I may therefore be allowed to refer to some former experiments of mine made at Hohenheim, and published in detail (*Landw. Versuchs.-Stat.*, **25**, 1880, 447—463; and *Bied. Centr.*, 1880, 724—729).

The investigation embraced "quantitative experiments" with mangold leaves, which, immediately upon cutting, had been weighed and stamped in a silo. The total fresh weight of the leaves amounted to 25,000 kilos. In the midst of the silo, and completely surrounded by leaves of the same kind, but separated from the adjacent mass, a carefully taken sample of 250 kilos. was buried and treated in the same manner as the whole silo: the latter had been simply cut in the soil, which consisted of a sandy clay. Owing to the pressure exerted on the leaves by stamping them in, and by a large mound of earth over the silo, a considerable quantity of juice was

sure to be pressed out and to flow off into the soil. I therefore filled several jars with weighed samples of leaves, closed them with sheet india-rubber, and buried them also in the silo in the midst of the other leaves. The jars were thus exposed to the same conditions of temperature as the other parts of the silo, but they did not admit of any loss of their contents. The leaves were left in the pit from the 19th of October, 1879, till the 10th of March, 1880, when they were taken out and analysed. The following was found to be the percentage composition of the dry matter:—

	Original leaves.	Ensilage. Out of the jars.	Ensilage. Out of the silo.
Crude protein (N × 6·25)	26·71	23·56	21·23
Ether extract	2·75	7·94	8·79
Fibre	13·84	11·55	18·31
Non-nitrogenous extract	38·28	34·77	39·67
Mineral matter (free from C and CO_2)	18·42	22·18	12·00
(Triglycerides)	(2·59)	(3·20)	(5·02)
Total nitrogen	4·274	3·765	3·397
Albuminoïd nitrogen	3·036	1·518	1·850
Nitrogen in peptones	none	0·295	0·092
Nitrogen in amides, &c.	1·058	1·952	1·455
Nitrogen in nitric acid	0·130	none	none

The following figures will show how much of each component of the dry original leaves was left in the ensilage after a complete and normal fermentation:—

	Original leaves.	Ensilage. Out of the jars.	Ensilage. Out of the silo.
Dry matter	100·0	82·00	50·64
Total nitrogen	4·274	3·087	1·907
Albuminoïds	19·29	7·78	5·82
Peptones	none	1·51	0·29
Non-albuminoïd nitrogen	1·058	1·601	0·737
Nitric acid	0·502	none	none
Fibre	13·84	9·47	9·27
Triglycerides	2·59	2·62	2·54
Mineral matters	18·42	18·19	6·06

Hence of 100 parts of each constituent, the following loss (—) or gain (+) had occurred during storage:—

	Jar ensilage (unpressed).	Silo ensilage (pressed).
Dry matter	− 18·0	− 49·4
Total nitrogen	− 27·8	− 59·8
Albuminoïds ..... } Peptones ..... }	− 51·8	− 68·3
Non-albuminoïd nitrogen	+ 51·3	− 30·4
Nitric acid.....	− 100·0	− 100·0
Fibre	− 31·6	− 33·7
Triglycerides.....	+ 1·2	− 1·5
Mineral matter	none	− 66·5

The amount of loss or alteration caused by the fermentation alone is seen from the first column. *More than half the albuminoïds had been decomposed*, whilst there was no loss nor increase of true fat, and 31·6 parts out of 100 of the fibre had been dissolved or removed. That the fermentation in the silo had taken place in just the same manner as in the jars, is proved by the fact that the loss of fibre is the same in both cases. The fat had not undergone any diminution nor increase. In consequence of the high pressure, much more of the soluble components had been lost from the leaves in the silo than from those in the jars.

The report above referred to, moreover, contains determinations of the *oxalic acid* and *complete ash analyses* of the fresh leaves and of the ensilage prepared from them.

It appeared to me peculiar that so *much nitrogen* (27·8 *per cent.*) *had been lost** during the fermentation in the jars; and I therefore resumed this investigation in Japan with my assistant, Mr. J. Sawano, and we have found that the largest portion of *this loss is caused by the preparatory drying of the ensilage* before reducing it to a proper powder: ammoniacal organic compounds are volatilised when drying the sour fodder, probably by dissociation of some organic salts (ammonium lactate). A report on this investigation will be published ere long in *Landw. Versuchs.-Stat.*, edited by Professor Nobbe.

* Prof. Kinch observed a loss of about 13 per cent. of the total nitrogen.

OBITUARY NOTICES.

ROBERT ROSCOE FELIX DAVEY was born about 1842, in London, where he spent his earliest childhood. At first he was a very healthy and strong child. When seven years of age he contracted rheumatic fever, and he became and remained very delicate until his death. When nine years of age he devoted himself to studies of a serious nature, and it was difficult to get him to take sufficient relaxation from them. In 1854 he went abroad with his friends, and remained there until 1857, when he came to London to finish his education, and at 18 years of age he entered the War Office. He was an accomplished linguist, being acquainted both with modern and ancient languages. He was a man of great amiability of character, and very fond of science. About seven years before his death he married Miss Mary Vincent, by whom he leaves one daughter.

He was elected a Fellow of the Chemical Society in 1867.

JAMES HOGARTH, by whose premature death science has lost an ardent student, was born in Ardrossan, on 17th November, 1858. Ever diligent and painstaking, he obtained the medal as best scholar in the Ardrossan Public School, and later several medals were awarded him at the Irvine Academy. A desire to know more of the material universe induced him to enter the laboratory of Dr. Milne, of Glasgow, as pupil and laboratory assistant: after having held this position 18 months, and as his taste for chemical science was confirmed, he determined to take up a more complete course of study. He accordingly entered the technical laboratory of Anderson's College, Glasgow, and studied there for two years, under Dr. E. J. Mills, F.R.S. While there, besides going through the usual course of study, he conducted investigations under the guidance of Dr. Mills, on "Chemical Equivalents," and on "Lactin" (*Proc. Roy. Soc.*, No. 192, 1879). After completing his studies, and eagerly desiring to continue as an investigator in pure science, he entered the employment of Mr. J. B. Hannay, of Glasgow. Here Mr. Hogarth's aptitude for experimental investigation, as well as his eagerness to work at pure science, soon caused him to be occupied entirely with chemical and physical research, and he was engaged with Mr. Hannay in the work which culminated in the discovery that solids are still soluble in fluids which have passed

their critical temperatures, and thus entered the gaseous state. ("On the Solubility of Solids in Gases," *Proc. Roy. Soc.*, **30**.)

Mr. Hogarth became convinced, however, that the pursuit of pure science would never lead one who has his place to gain in the world to a position of affluence; he determined therefore to enter more into the commercial side of science, and in January, 1880, he became assistant to Dr. Vaughan, of Providence, Rhode Island. Somewhat disappointed here, he became engaged upon United States Government work, with Mr. Blair, at Newport, R.I., and lastly was working under the firm of Booth, Garrett, and Blair, in Philadelphia, when his last illness came upon him.

By the death of Mr. Hogarth, chemistry has lost a most devoted student and painstaking investigator, and though cut off at the early age of 24, he had shown that had life and opportunity been afforded him, his best energies would have been spent in the service of science. His anxiety to prosecute investigation, and the delight he felt in such work were so great, that when an investigation on which he was engaged was arriving at its most important stage, he would go to work early in the morning and stay in the laboratory till a late hour at night, and only leave when nature imperatively demanded repose. Although his short life was devoted to chemistry, he yet had that wide interest which all true lovers of nature find in every branch of science and art. Generous in his impulses, always striving to feel in harmony with those associated with him, and with a great reverence for all that nature can teach us, he is mourned by those who had the happiness to share his companionship, as a friend whose presence rendered all labour sweeter, and whose hopeful converse tended to raise the mind from dwelling on the grim side of life to a more sunny contemplation of the future.

Edward Hunt was born about 1830, at Hammersmith, and studied at University College, London, where was laid the foundation of his future extensive knowledge of chemical science. Shortly after this he went to Manchester, and was for a time engaged as assistant to the late Mr. Crace Calvert, in the laboratory of the Royal Institution. After being there for some little time, he became acquainted with Mr. H. D. Pochin, of the firm of Messrs. H. D. Pochin and Co., manufacturing chemists, Salford and Manchester, and from that time to his death a very intimate relationship existed between them. It was in the laboratory in Quay Street, in the year 1857, while working with Mr. Pochin, that the important discovery was made of the process by which rosin could be distilled without decomposition. For that discovery a patent was taken in April, 1858. This patent was afterwards put into very extensive working at Runcorn Gap, and for a consider-

able period a very large portion of the rosin used for the production of pale yellow soaps was made by that process. The patent when in full work was sold to the Messrs. J. and T. Johnson, of Runcorn, for, as we believe, a considerable sum of money.

Mr. Hunt and Mr. Pochin, about the year 1861, joined Mr. S. Barlow as partners in the important bleaching, dyeing, and finishing works, conducted at Stakehill, near Middleton, which partnership continued until the death of Mr. Hunt.

During the last years of Mr. Hunt's life, he devoted the whole of his time to a consideration of chemical questions bearing upon the industrial operations conducted in Manchester and its neighbourhood, his knowledge of which probably was not second to that of any existing chemist. He made many suggestions and improvements which were valuable in connection with his own business at Stakehill, and was engaged in many important trials involving very large interests, in which it was necessary to establish the effect of many of the processes connected with paper-making, bleaching, dyeing, and finishing of cloths for the market. The effect of certain processes in elastic web-making was established by a most elaborate inquiry. In all such cases, the loss of Mr. Hunt to the district of Manchester will be severely felt. We know of no one who can for many years supply his place.

He died at his residence in Manchester, on Sunday, the 12th of August, after a painful illness, extending over a period of nearly 12 months. He was elected a Fellow of this Society in December, 1851.

William Henry Aston Peake, son of John Shaw Peake, Deputy Crown Solicitor, was born at Dublin, on March 28, 1855. After having received a good general education, he commenced the study of chemistry under Professor Galloway. In 1873 he became assistant to Professor Reynolds, being chiefly occupied in preparing lecture experiments. In 1874 he came to England, and for about a year acted as assistant to Professor McLeod, at the Royal Indian Civil Engineering College, at Cooper's Hill. He was afterwards assistant to Mr. Cromwell Varley. In 1878 he became Assistant in the Rothamsted Agricultural Laboratory, where he remained till January, 1882. While here he communicated to the Society, in conjunction with Mr. Warington, a paper "On the Determination of Carbon in Soils." The results there arrived at have since been amply confirmed by G. Loges. Early in 1882 he left England to fill the chair of Chemistry and Physics in the College at Stellenbosch, Cape Colony. His health had for some time been precarious, and it was hoped that the change of climate would prove beneficial to him. This hope was, unfortunately, not

realised. He gradually sank, and died of pulmonary consumption, on June 28, 1883.

Mr. Peake was an ardent lover of science. His knowledge was extensive, and included an acquaintance with several oriental languages. Professor Reynolds says:—"Of his personal character I cannot say too much. I have rarely met with a man of so amiable a disposition, or one more modest and unassuming, who possessed as varied and extensive knowledge."

Mr. Peake married in 1876 a daughter of the Rev. Dr. Sexton. He leaves a widow and three children. He was elected a Fellow of the Society on May 4, 1882.

William Plunkett received his general education in a private school in Dublin; on leaving school he became a clerk in the office of the Drogheda Railway Company. Having a great love for knowledge he attended during this period the evening Practical Chemical Classes, carried on in the laboratory of the Government Institution, then called the Museum of Irish Industry, now the Royal College of Science. At the end of his fourth session (1858–59), the post of Assistant Chemist becoming vacant through the death of the assistant, the Professor, Mr. Galloway, recommended the Director of the Institution, Sir Robert Kane, LL.D., to appoint Mr. Plunkett assistant. The Director acceded to Mr. Galloway's wishes, and the deceased Fellow continued to fill this appointment up to the time of his death.

During his studentship he suggested in a paper he contributed to the *Chemical Gazette*, the employment of sodic hydric tartrate in the place of tartaric acid as a test for potash. In 1875 he and the late Dr. Lancelot Studdert, LL.D., who was studying chemistry in the laboratory, contributed a paper to the Royal Irish Academy, "On the Mineral Constituents of the Lisdoonvaina Spa." The paper was published in the Proceedings of that Society. The Council of the Academy granted the authors £30 out of the Government Grant to carry out the research. In 1877 he and Dr. Studdert contributed a paper to the Academy "On the Solid and Gaseous Constituents of the Mallow Spa, in Co. Cork;" this paper was also published in the Proceedings of that Society, the Council of the Academy having allotted them £25 out of the Government Grant to carry out the research.

He was elected a Fellow of the Society in January, 1860.

The deceased Fellow was untiring in the discharge of his official duties, and he was greatly esteemed and respected by his colleagues and the students.

George Borwick Robertson was born at Dundee, on June 1st, 1831.

Little is known of his early life, but when 24 years of age he entered the Inland Revenue Department. At that time, it was necessary that a certain number of officials should be efficient chemists, to detect the adulteration of commodities chargeable with duty, and whatever might have been the previous chemical knowledge of the persons selected, they were sent to University College for two or three years to prosecute their studies. Mr. Robertson was one so selected, and after the completion of his University course we find him engaged in checking and supervising the manufacture of the bronze coinage at Birmingham.

When this work was completed he was engaged as Superintendent in the Stamping Department, at Somerset House, where his chemical knowledge was available for State purposes.

In May, 1872, he became Deputy Controller of that Department, and Controller, in 1876.

For some years before his death he suffered severely from diabetes, and on the 1st December, 1882, he died from that complaint.

As a Government servant he was precluded from publishing any investigations he made on subjects connected with his daily work, but his ability was recognised, and his rapid promotion showed that his official conduct was properly appreciated.

He was elected a Fellow of the Society on April 6, 1865.

Major-General Henry Young Darracott Scott was born at Plymouth in January, 1822. His father, Edward Scott, Esq., was the owner of large quarries in the neighbourhood, and was much respected by all who knew him.

He had five sons—the second, Captain Scott, R.N., the inventor of the patent gun carriage; the youngest, Thomas Scott, distinguished himself at Cambridge; and the fourth, the subject of this memoir, entered the army as Second Lieutenant of the Royal Engineers, December 18th, 1840.

Whilst a cadet at Woolwich, he had the advantage of having General Harness as an instructor, for which he ever felt grateful, and with whom he formed a friendship which only terminated with death. He was presented with the good conduct sword on leaving.

He joined at Chatham at the beginning of 1841, and remained there for about fifteen months. He was then stationed for a few months at Woolwich, and afterwards at Plymouth, and in 1843 he was ordered to Gibraltar, where he filled the office of adjutant. On December 19, 1843, he was promoted First Lieutenant.

He was promoted to be Second Captain on November 11.

In 1851 he was appointed Senior Instructor at Woolwich.

Besides his regular work at the Academy, in which he was already

beginning that inquiry into the "representation of ground in plans," which he afterwards perfected at Chatham, he also commenced his more favourite study of chemistry in connection with building works; and in a little laboratory which Colonel Sir W. Reid, then C.R.E. at Woolwich, got for him, he made his first experiments in sulphurising limes; the results of which were most successfully used in a little powder magazine then building in the Arsenal.

He had started the laboratory with the excellent object of inducing the young officers of Royal Engineers stationed at Woolwich to study the chemical examination of materials connected with building; and that large-minded commander, Sir W. Reid, encouraged it by being the first to go there and practise under Scott.

Chatham afforded him greater facilities in carrying forward and developing those discoveries in limes and cements which had occupied his mind at Woolwich. Having charge of the Laboratory, he not only tried experiments there, but entered into an agreement with Messrs. Lee and Smith, of Snodland, on whose premises he erected a kiln, where he was able to carry them out upon a larger scale.

Upon this subject Major-General Collinson writes: "He had charge of the Chemical Laboratory, and in this his ceaseless thoughts and labours perfected the idea of the 'Selenetic Lime;' in the final form of the invention it was produced by grinding sulphate of lime with any good slightly hydraulic lime, after burning. This was a novel idea, and in the way it was done had a true chemical effect of making the lime much more hydraulic, and of remarkable strength and yet at a comparatively cheap rate; he took out patents for these, which are now being worked by a company in London. Owing, however, to certain commercial obstacles in the lime trade, the invention has been slowly taken up, but it has been used in some important cases with good effect, particularly at the Royal Albert Hall, the Alexandra Palace, and the new Law Courts in London; and whenever it is properly made and properly used I believe it will be found to be an extremely valuable addition to the building material of the country. But unfortunately for General Scott the difficulties have hitherto been too great to give him any satisfactory return for his long labours; as, in many other cases, the results of his ingenuity and toil will be reaped by others."

It is a matter of regret that General Scott has left so little in writing respecting his discoveries on various subjects; his contributions, however, which appeared from time to time in the *Professional Papers of the Corps of the Royal Engineers* are exceedingly valuable. Especially may be mentioned his "Observations on Limes and Cements," and "Concrete, a Substitute for Brick and Stone Masonry," which was subsequently issued in a separate form. He

also contributed some valuable papers "On the Representation of Ground."

On May 19, 1863, he was promoted Brevet-Major, and on December 5 the same year he became a regimental Lieutenant-Colonel.

On December 14, 1865, he was seconded for employment under the Commissioners of the Great Exhibition of 1851, and took up his appointment at South Kensington.

The chief work by which General Scott will be recorded at Kensington was the construction of the Royal Albert Hall, with the design and execution of which he was entrusted in 1866.

The general idea for this building had been left by Captain Fowke—what Scott did was to apply it to the ground; in the course of which problem he found it necessary to entirely alter the size and interior arrangement of the building, and it virtually became his own design.

He was promoted Brevet-Colonel on June 7, 1871, and on August 19 the same year he retired from the service with the honorary rank of Major-General, but he continued to be employed at South Kensington. He was for some years employed as Examiner in Military Topography under the Military Education Department. He was appointed a Companion of the Bath on May 20, 1871, and in June, 1875, he was elected a F.R.S.

We must here briefly refer to his sewage system, which seems to have been more successful than most. A company was formed, with the Duke of Sutherland as chairman, for working it; and though it has not been commercially remunerative, its want of success has not arisen from any default in its chemical efficiency, but solely from the difficulty of moving corporations and the other public bodies who have the responsibility of the public health in their hands. Not only is the public health in question, but the great national want of a high class fertiliser for the land, and it may be hoped and expected that though he did not live to see it and to reap the advantages he so well deserved, General Scott's inventions may yet have a great success, and be brought into common use.

Another of General Scott's inventions was the conversion of lime into cement by what he called the Selenitic method, as to which Professor Abel, in his official report on the scientific inventions exhibited in the International Exhibition of 1871, remarks: "There are few scientific inventions now exhibited which give promise of becoming of greater practical importance than that of the Selenitic mortar of Major-General Scott, and which is the latest and decidedly the most useful of the numerous results obtained by that officer in the course of the valuable researches, both scientific and practical, which

he has carried on for many years past on the nature, productions, and applications of cements and hydraulic limes."

This brief record gives but a very poor idea of his work; we have said nothing respecting his efforts to induce Her Majesty's Commissioners to take up technical education and the partial success of those efforts, nor of his gratuitous labours in connection with the Metropolitan Association for Improving the Dwellings of the Industrial Classes, constructing blocks of buildings, and superintending the works. "In a word," writes one who knew him well, "Scott's whole life was that of devotion to work for the benefit of the public service, or the advancement of scientific knowledge. He was so engrossed with his thoughts and labours on the many practical subjects he took up, that he paid very little attention to the steps necessary for securing any benefit to himself."

Peter Spence was born at Brechin in Scotland, and began his business life at Perth. His education, although good of its kind, was limited in its range and included little or no scientific teaching. He, however, early showed a liking for chemistry, and whilst an apprentice at Perth he applied his spare time to the study of that branch of science. In the year 1834 he began business at Greenwich as a chemical manufacturer. Subsequently he took the control of some chemical works near Carlisle, and here in 1845, by a patient course of experimenting, he discovered a process for the manufacture of alum from the refuse shale of collieries and the waste ammoniacal liquor of gas-works. This discovery was the foundation of his success. After patenting his process, he left Carlisle and came to Manchester, choosing this city because the raw materials of his manufacture could here be readily obtained, and because the district supplied a good market for the finished article. One practical result of his invention was to lower the price of alum from 30 to 40 per cent., but it did not prove an immediate financial success. A good many difficulties had to be overcome and some heavy losses sustained before much benefit was reaped by the inventor. The Pendleton Alum Works, by successive extensions, have now become the largest in the world, being capable of turning out 200 tons of alum per week, besides other products. In addition to these works Mr. Spence also established chemical works at Goole and at Birmingham. Since he introduced his process, the manufacture of alum, as of chemical substances generally, has undergone many changes. A number of these changes were the result of Mr. Spence's own researches. He took out between 50 and 60 patents, nearly all of which were for improvements in chemical processes. He was, indeed, looked upon as one of the best practical chemists of the day, and he obtained this

distinction by hard work in the laboratory. In the course of his scientific experiments, Mr. Spence found amongst other things that steam of 212° F. could be made to raise the temperature of saline solutions to their boiling point, however high that might be. Thus a solution of acetate of potash might be readily raised by open steam to a temperature of 336° F. A paper on the subject was read by Mr. Spence at the Exeter meeting of the British Association. His statement was doubted by the chemists present until by actual experiment he proved the truth of what he had advanced. About 10 years ago, the circumstances of an accident on one of the English railways, which seemed to indicate that cold increased the liability of cast iron to fracture, led him to undertake a series of experiments on cast-iron bars at zero (F.), and he found that instead of being weakened by reduction of temperature the resistance of the iron to fracture was in fact increased some 3 per cent. A similar investigation made at the time by Dr. Joule gave substantially the same results. The purification of the air of towns was a subject which he had studied. He brought before the Manchester Literary and Philosophical Society, of which he was an active member, a scheme for purifying the air of a town by conducting the smoke of all house and factory chimneys along the sewers and up a column some 600 feet in height, at which altitude he believed the law of the diffusion of gases would operate to prevent any injury to public health. The author firmly held to the theory that when smoke is completely consumed it is only the mechanical impurities which are removed, and that sulphuric acid, the element most injurious to life, remains. If his scheme did nothing else it helped to attract attention to the means of carrying away that most insidious domestic poison, sewer gas. Amongst Mr. Spence's patents is one for a furnace for calcining sulphur ores and condensing the sulphurous acid produced. This furnace has been adopted at the great copper works at Swansea, where the ores were previously burnt in the open air, to the great detriment of vegetation.

Mr. Spence was an earnest advocate of temperance. A total abstainer from his youth, there was probably no cause in which he took a keener interest; to all public objects of which he approved, he gave most liberally. His private gifts of a charitable nature were also upon a very generous scale. He was a county magistrate, and held several other public positions.

He was a man of strong Christian principles, and a naturally sanguine and buoyant temperament, and thus repeatedly fought his way out of reverses which would have crushed other men.

Mr. Spence's first wife was Miss Agnes Mudie, of Dundee, and of their family of eight children seven are now living. He was elected a Fellow of this Society in 1862.

Charles William Siemens was born at Lenthe, in Hanover, on the 4th of April, 1823. He was educated at the Gymnasium of Lübeck, the Polytechnic School of Magdeburg, and finally studied under Wöhler and Himly in the University of Göttingen. In 1842 he became a pupil in the engine works of Count Stolberg; his pupilage was, however, of short duration, as we find him next year in England, where having had the good fortune to receive an introduction to Mr. Elkington of Birmingham, he disposed of the joint invention of Dr. Werner Siemens and himself in electro-gilding. Next year he returned to England with another invention of the brothers—the chronometric governor, which obtained him an introduction to the engineering world, and determined him to reside in England. A little later he introduced the anastatic process for the reproduction of old or new printed matter. Caustic baryta was first applied to the printed matter to convert the resinous ingredients of the printing ink into an insoluble soap, the stearine being precipitated with sulphurous acid. The printed matter could thus be transferred by pressure to zinc. Next year, 1846, he constructed a double cylinder air-pump.

But these are almost forgotten inventions now, having been totally eclipsed by those larger industries in which for years past his inventive faculties have been exercised; we refer of course to his regenerative gas furnaces and steel processes, which are specially interesting to the Fellows of this Society.

At the time that he turned his attention to the science of heat, the philosophers of the day were not agreed as to the nature of heat, but after having read the disquisitions of the modern theorists, he finally determined in his own mind that heat was a form of energy, and considered its different applications from this thoroughly philosophical point of view. From a paper which he read later, in 1853, before the Institution of Civil Engineers, "On the Conversion of Heat into Mechanical Effect," it is evident he had already grasped the two methods of obtaining the best results from an actual engine, viz., by carrying expansion to the furthest possible limit, or by the application of regenerators, and he used the latter as the most practicable. His first application of a regenerator was to a 4-h.p. engine, which he constructed in 1847 in the factory of Mr. John Hick, of Bolton, having a condenser provided with regenerators, and using superheated steam. He made and exhibited other such engines, but owing to the difficulty of working with superheated steam, the application of the regenerative principle to motor engines had to be abandoned.

It was about 1856 that in connection with his brother, and then pupil, Mr. Frederick Siemens, he experimented with regenerators applied to furnaces. The first experimental furnace was erected that year in Scotland Yard, and was partially successful with solid fuel.

Experiment after experiment had to be made, until in 1862 the brothers brought out the regenerative gas furnace, which is now used throughout the civilized world.

Having thus a means of obtaining intense heat, he looked upon his furnace as capable of accomplishing what Reaumur, and after him Heath, had proposed to do, namely, to produce steel in large quantities upon the open hearth, by fusing cast or pig metal with wrought metal or scrap, although the general opinion of practical men was opposed to the idea of accomplishing the object. Furnaces were erected both here and in France, but it was only after he had erected his Experimental Steel Works at Birmingham that what is now known as the open-hearth steel process was acknowledged to be a success. Sir William's two lectures before the Chemical Society, that on "The Regenerative Gas Furnace as applied to the Manufacture of Cast Steel" (*Chem. Soc. J.*, 1868, **6**, 279—310), and "On Smelting Iron and Steel" (*ibid.*, 1873, **11**, 661—678), refer at length to these inventions. At the time he was making his experiments at Birmingham, one of his licensees, M. Martin, of Sireuil, also succeeded in producing steel on the hearth of one of Sir William's regenerative gas furnaces. The two processes are now worked together, the Siemens or ore process being that in which ore is dissolved in a bath of cast iron, and the Siemens-Martin or scrap process, that in which scrap is so dissolved. In the latter of the two lectures above referred to, another invention of Sir William Siemens is described, a direct process for the reduction of pure iron from the ore mixed with fluxing and reducing materials by means of a rotary furnace in which a high temperature is first produced by the combustion of gas and heated air within the same, and then after the batch is raised to a red heat, reaction between the carbonaceous matter and the ore takes place, carbonic oxide being developed, which combines with the heated air. The heat rises rapidly, and fusion of the earthy constituents of the ore occurs simultaneously with a continuance of the reducing action. After the liquid mass of cinder is removed, the rotator is made to revolve more quickly, and an agglommeration of the metallic iron in the form of balls is effected, which has been found to be nearly chemically pure.

In 1868 he read a paper on "Puddling Iron" before the Chemical and Mechanical Sections of the British Association at Norwich, in which, as the result of experiment and observation, the author "ventured to assert that the removal of the silicon and carbon from the pig iron in the ordinary puddling or boiling process, is due entirely to the action of the fluid oxide of iron present, and that an equivalent amount of metallic iron is reduced and added to the bath."

As an aid to chemical work in large applications of heat, we may refer to his electrical resistance thermometer and pyrometer, which formed the subject of the Bakerian Lecture to the Royal Society in 1871, and has since been published in the *Journal of the Society of Telegraph Engineers*, **3**, 297—338.

Having thus referred briefly to a portion of Sir William Siemens's work in connection with chemistry and metallurgy, it only remains to give the titles of some of the many papers which he read before different Societies, so as to give an idea of the many-sidedness of his mind and works. The principal of these not already referred to are—"The Electrical Tests employed during the Construction of the Malta and Alexandria Telegraph, and on Insulating and Protecting Submarine Cables," read on May 20th, 1862, before the Institution of Civil Engineers; "Observations on the Electrical Resistance and Electrification of some Insulating Materials under Pressures up to 300 Atmospheres" (*Brit. Assoc. Rep.*, 1863, 688—694); "On Uniform Rotation" (*Phil. Trans.*, 1866, **156**, 657—670); "On the Conversion of Dynamical into Electrical Force without the Aid of Permanent Magnetism" (*Proc. Roy. Soc.*, 1867, **15**, 367—369); "The Action of Light on Selenium," a lecture read to the Members of the Royal Institution on the 18th February, 1876; "On Determining the Depth of the Sea without the Use of the Sounding Line" (*Phil. Trans.*, 24th Feb., 1876); "Utilisation of Heat and other Natural Forces," and "Gas and Electricity as Heating Agents," lectures read before the Glasgow Science Lectures Association in 1878 and 1880; a series of papers on the "Influence of Electric Light on Vegetation" (*Proc. Roy. Soc.*, 1880; *Brit. Assoc.*, 1881); "The Dynamo-Electric Current and Certain Means to Improve its Steadiness" (*Phil. Trans.*, 1880); "On the Use of Coal-gas as a Fuel," Society of Chemical Industry, 29th June, 1881; "Science and Industry," an address delivered before the Birmingham and Midland Institute 20th October 1881; "On the Conservation of Solar Energy" (*Proc. Roy. Soc.*, 20th February, 1882); this paper, with a translation of the discussion on the subject which took place before the Academy of Sciences of Paris, has been brought out as a separate work by Messrs. Macmillan; "On a Deep Sea Electrical Thermometer" (*Proc. Roy. Soc.*, 7th June, 1882); "The Electrical Transmission and Storage of Power" (*Proc. Inst. Civ. Eng.*, 15th March, 1883); "On the Dependence of Radiation on Temperature" (*Proc. Roy. Soc.*, 25th April, 1883).

Besides these papers Sir William gave several valuable inaugural addresses, when elected President of the Institution of Mechanical Engineers, twice of the Society of Telegraph Engineers, of the Iron and Steel Institute, of the British Association, and Chairman of the Council of the Society of Arts.

He obtained the Gold Medal and afterwards the Albert Medal of the Society of Arts; the Telford prize and premium, and the Howard quinquennial prize of the Institution of Civil Engineers; the Bessemer Medal of the Iron and Steel Institute; together with prize medals at the Exhibitions of 1851 and 1862, and the Grand Prix at the French International Exhibition of 1867, for his regenerative gas furnace and his method of making steel. In March last year he received the honour of knighthood in official recognition of his great scientific services. He was connected with many of the leading Societies abroad, and various foreign orders, including the Legion of Honour, were conferred on him.

In 1858 he established with his brothers, Dr. Werner and Mr. Carl Siemens, the telegraph works now known as Siemens Brothers and Co. Limited. From them telegraph lines have been shipped to various quarters of the globe. The Indo-European telegraph line was constructed by them in connection with their Berlin house, as also the North China Cable. The Platino-Brazilian cable, the Direct United States cable, that for the Compagnie Française du Télégraphe de Paris à New York. The two "Gould" cables, laid for the American Telegraph and Cable Company, have been laid by this enterprising firm during the last 10 years, whilst they are under contract to lay two further cables across the Atlantic. Besides being the Chairman of this Company, Sir William was connected with many other commercial undertakings, such as the Landore Siemens Steel Company, the Indo-European Telegraph Company, the Leipzig Tramways Company, and others, whilst he was an active member of the Councils of most of the learned Societies with which he was connected.

He died on the 19th November, 1883, after a few days' illness, and was buried at Kensal Green Cemetery on the 26th of that month, after a public funeral service at Westminster Abbey.

James Hill Smith, of Plymouth, who died on the 8th of October, 1883, aged 25 years, was elected a Fellow in January, 1882. He showed very early in life a great natural ability and love for science, especially for experimental chemistry, to which he devoted much of his leisure hours. After studying at the Local School for Science, where he earned many prizes in connection with South Kensington, he went to Owens College, Manchester, attending the lectures of Professors Roscoe and Schorlemmer. After passing through the usual three years' course of training, he was appointed, at the age of 23, Demonstrator of Chemistry at the University College, Nottingham, under Dr. Clowes, which appointment he had to relinquish in consequence of his health giving way under the pressure of the duties which devolved upon him. Mr. Smith was a young man of much

promise, as is shown by the testimony of the Professors under whom he studied.

He was elected a Fellow of the Society on May 4, 1882.

WILLIAM SPOTTISWOODE was born in London, January 11, 1825. He belonged to an ancient Scottish family, many members of which have risen to distinction in Scotland and also in the New World. He was first sent to a private school at Laleham, under Mr. Buckland, brother of Dean Buckland; thence he was removed to Eton, where, however, his stay was short. He with his brother then went to Harrow, then under the rule of the present Bishop of Lincoln; here he was a very studious, quiet, and thoughtful boy, not much given to athletic games. He remained at Harrow three years, and in 1842 obtained a Lyon scholarship. In this same year, he entered Balliol College, Oxford; here he showed an extraordinary liking for mathematical studies. His power of work was very great, and his industry equally so. In 1845 he took a first class in mathematics, and he afterwards won the Junior (1846) and Senior (1847) University Mathematical Scholarships. He returned to Oxford for a term or two, and gave a course of lectures in Balliol College on Geometry of Three Dimensions. He was examiner in the Mathematical Schools in 1857—58. On leaving Oxford he took an active part in the working management of the business of the Queen's printers, about this time resigned to him by his father, Andrew Spottiswoode, brother of the Laird Spottiswoode, and the business largely developed under his hands.

At an early age he studied languages, both Oriental as well as European, and in 1856 he made a journey through Eastern Russia, of which he published a graphic account in his book entitled "A Tarantasse Journey through Eastern Russia in the Autumn of 1856." In 1860, in company with his sister and brother, he went through Croatia and Hungary. In 1861 Mr. Spottiswoode married the eldest daughter of the late William Urquhart Arbuthnot. His exceptional qualifications as an organizer have not only served to advance his business in the way before mentioned, but, together with the broad and liberal education on which they were based, combined to raise him to the high position he held in science. He was long connected with the Scientific Societies of this country, which have benefited by his sound judgment and the high motives by which he was actuated. He had much sympathy with the workmen in his large establishment, who have lost in him a true and trustworthy friend. He was elected a Fellow of the Royal Society in 1853. He was Treasurer of the British Association from 1861 to 1874, and of the Royal Society from 1871 to 1878, President of the British Association, 1878, and of the

London Mathematical Society, 1870—72. He was elected President of the Royal Society in 1879, which office he held until his death. He was LL.D. of the Universities of Cambridge, Dublin, and Edinburgh, D.C.L. of Oxford, and in addition to these honours he had many literary and scientific distinctions. He was elected a Fellow of the Chemical Society in 1879. Of late years he has divided his attention between mathematics and physics, his work in the latter field being devoted more especially to polarised light and electrical phenomena. It would be out of place here to refer to his numerous and important mathematical and physical papers, except to say that they showed that he occupied a place in the front ranks of workers on these subjects.

Mr. Spottiswoode was a man of deep sympathy and great sensitiveness, yet possessing a clear judgment and rapid decision, and also great patience and courtesy. He was beloved by all who knew him. He died of typhoid fever on June 27th, 1883, and was buried in Westminster Abbey. In his death science has sustained a great loss.

James Thomas Way was the son of a physician of repute at Tonbridge Wells. In 1841 he entered as a pupil the laboratory of the late Professor Graham at University College, and was afterwards for some time his assistant, and was one of the earliest Members, although not an original Member, of the Chemical Society. In 1843 he was asked to assist the late Dr. Daubeny, Professor of Chemistry at Oxford, in some investigations on the influence of light upon growing plants, and acting on the advice of Professor Graham, he remained with Dr. Daubeny for about two years, forming with him a close friendship. In 1844 the Royal Agricultural Society of England proposed to carry out a series of analyses of all agricultural plants grown for the purpose, of every variety and under every attainable variation of soil and climate, in the United Kingdom. This investigation was entrusted to Professor Way and Mr. G. S. Ogston jointly, and the results were published in the several numbers of the Society's Journal, extending over the period between 1846 and 1850. In the earlier year, Way was appointed Professor of Chemistry at the Royal Agricultural Society at Cirencester, which appointment he retained until 1847, when he became Consulting Chemist to the Royal Agricultural Society of England, in which position he had the opportunity of doing an infinite variety of valuable work, and greatly adding to our knowledge of the chemistry of agriculture. He was appointed a member of the first Commission on Rivers' Pollution, and for the purposes of their Report acquired a vast amount of information upon a subject of which little or nothing was at that time known. A second Commission was appointed, about 1864, of which Way was also a member,

for a continuation of the work of obtaining a knowledge of the various forms of pollution to which our rivers are subjected, with a view to legislation, but shortly after this his health began to fail, and this prevented him from being able to do any very great amount of active work, his time being devoted as much as possible to such work as was necessary for the purpose of enabling him to give evidence before Parliamentary Committees, in which he was from time to time engaged. At the time of his death he had just been examined, on the part of the Corporation of the City of London, on the condition of the River Thames. He was married, and leaves a widow with three children. He was a staunch friend and a loyal colleague, and amongst those who have been associated with him it will be said that no one was more scrupulously accurate in his work than he.

Perhaps one of the most important works in which Way was engaged was connected with his observation of the power possessed by soils to absorb and retain alkaline salts from solution. His first paper on this subject, in 1850, attracted great attention, and has undoubtedly led to results of the highest importance. A second paper on this subject, in 1852, was of much interest, as giving an explanation, founded upon experiment, of the condition in which the alkalis and ammonia are retained in the soil, viz., as double silicates; and a third paper, upon the effect of the addition of lime, and its fertilising influence upon the soil, completed the work in this direction. Elaborate work on the "Phosphoric Strata of the Chalk Formation" occupied much time, and was conducted in conjunction with the late J. M. Paine, of Farnham. Then "The Atmosphere as a Source of Nitrogen to Plants" involved an important investigation, and some analytical work on new methods of the estimation of nitric acid and ammonia in waters gave the best results attainable in those days. All this, and an infinite variety of other work, from which it is difficult to make a selection, was published in the Royal Agricultural Society's Journal of about that date. He was an Honorary Member of the Royal Agricultural Society, an old Member of the Chemical Society, being elected in 1846, and was upon the Council of Institute of Chemistry. His age was 63.

James Young was the son of a working cabinet maker, who lived in the Drygate of Glasgow. He was born in the year 1811, and having obtained the rudiments of education, was apprenticed to his father. Whilst thus employed he began to attend classes at Anderson's College. One of his favourite studies was chemistry, and he especially attracted the attention of Professor Graham, then in the chair of Chemistry, who found him useful in making for him pieces of apparatus, and in otherwise assisting him. Ultimately he relinquished his

trade of cabinet maker, and was installed in a subordinate capacity in the University, where he remained for seven years, acting latterly as assistant to Professor Graham, and occasionally lecturing in his absence. On Graham's removal to University College, London, Young accompanied him, and was again associated with him in his work, continuing the while to extend his own acquirements, and to cultivate his taste for original investigation and research. After remaining for about four and a half years in London, he was appointed, on the recommendation of Professor Graham, to a responsible position in the works of Messrs. Muspratt, at St. Helens, near Liverpool. Subsequently, about the year 1843, he removed to Manchester, where he was employed in the works of Messrs. Charles Tennant and Co. While he lived in Manchester Mr., now Sir, Lyon Playfair, M.P., whose acquaintance he had made at Anderson's College, brought under his notice the fact that there was oil flowing from a pit at Alfreton, in Derbyshire, and asked whether any use could be made of it. The question was one precisely of the kind to fire the inquiring spirit of James Young, for in all his labours he ever worked towards some practical result. He accordingly went and examined the oil spring, submitting the oil to an exhaustive series of experiments, with the result that in the year 1848 he, along with Mr. Meldrum, who had been his assistant in Manchester, established works for the purpose of preparing the product for the market, and it soon commanded a ready sale. Speedily, however, the spring became exhausted, and the experiment threatened to end in disappointment and failure.

About this time, the Torbane Hill mineral had begun to be used for gas-making, but being found to be too rich for the purpose, it was brought under the notice of Young, who, by distilling the mineral at a low temperature, succeeded in producing a considerable quantity of crude paraffin oil, and he at once saw that here he had found the substitute for his petroleum spring of which he had been in search. Having secured the patent rights of his invention, he then proceeded, in conjunction with Mr. Binney, of Manchester, and Mr. Meldrum, to erect works at Bathgate, in the centre of the Torbane Hill field, for the purpose of extracting the oil from the mineral; and here in the year 1851 was laid the foundation of what has now become an extensive and lucrative industry. Very soon the works at Bathgate were found inadequate to supply the growing demand for the products of the hitherto valueless shale, and a larger and more complete establishment was erected at Addiewell, near West Calder, where a deposit of shale had been found. But his success in experiments with shale did not end in the production of lubricating and burning oils, for, whilst it cannot be claimed for him that he was the discoverer of solid paraffin, it is acknowledged

that he was the first to produce it in quantity. He also devoted his attention to the construction of lamps in which the oil produced at his works could be consumed, thus leading the way in what has now become another important department of industry.

In the year 1866, shortly after the expiry of his patent rights, Young sold his whole works at Addiewell and Bathgate to a limited liability company. As showing the extent of the industry created by him, it may be mentioned that when the works at Bathgate and Addiewell were transferred to the limited company the total production of mineral oil in Scotland amounted to over six and a quarter million gallons a year. The entire production is now estimated at fifty million gallons.

James Young's name will be chiefly associated with the discovery of the method of distilling oil from shale; but he was also the author of other useful inventions. When he worked in the laboratory of Professor Graham, the making of caustic soda was an operation conducted on a small scale in silver vessels: Young discovered that iron vessels might be used instead, an observation of great importance in reference to alkali-making. The manufacture of chlorate of potash is also a large and growing industry; Young invented and carried into effect the method still in use in its production. He was also the first to suggest the application of caustic lime to prevent the corrosion in the hulls of iron ships, the course followed, we believe, in the Royal Navy. All these inventions belong to the period of his earlier life; but even in his later years he continued his favourite study. He was also much interested in the subject of electric lighting, and tried many experiments with the view to its practical application for ordinary purposes.

From his early connection with Anderson's College, he was led to take a special interest in the institution, and spent a great deal of time in promoting its interests. From 1870 till 1877 he was chairman of the trustees, and after his retirement he gave a donation of £10,500 for the foundation of the Young Chair of Technical Chemistry.

He was closely associated with Dr. Livingstone all through his life, and supported and encouraged him in his self-sacrificing labours in connection with the exploration of Africa.

He was a Fellow of the Royal Society, and received the honorary degree of LL.D. from St. Andrew's University. He was also one of the original Members of the Chemical Society. His death took place at his residence at Wemyss Bay, on May 13, 1883. He was in his 72nd year, and had been failing in health for some time. He is survived by three sons and four daughters.

LI.—*An Explanation of Gladstone and Tribe's "2-3 Law in Chemical Dynamics."*

By John W. Langley.

In the *Proceedings of the Royal Society*, **19**, p. 498, and also in the *Journal of the Chemical Society*, 1871, p. 1123, will be found a paper by Messrs. Gladstone and Tribe entitled "A Law in Chemical Dynamics." The authors show, by a record of experiments, that if a plate of metal is suspended in a solution of another metal which it can precipitate (the plate being hung so that it reaches neither to the top nor to the bottom of the liquid), the rate of chemical action, as shown by the loss of weight in the suspended plate (for a given period of immersion), will vary with the percentage strength of the solution of the salt in a remarkable manner, which they epitomise in the statement, that if the percentages of the salt be expressed by a series of the powers of 2, the chemical action will be expressed by the corresponding powers of 3, so that for percentages represented by 1, 2, 4, 8, &c., the rate of action will be 1, 3, 9, 27, &c. They further state that this law of action holds good up to about 3 per cent., and that for solutions weaker than this, they have demonstrated it through a range of from 1 to 1,000,000.

They also give for the law a mathematical expression which seems to have been defectively printed, for when the typographical errors are corrected I find it to be expressed by $\log C = \log p \frac{\log 3}{\log 2} + \log K$, where C is the rate of chemical action, p is the proportionate quantity of salt, and K is a constant. In the particular example given in their paper they employed a plate of copper suspended in a solution of silver nitrate.

The authors do not give any explanation of the law which they have discovered.

The following question at once arises. Is the rate of metallic precipitation for varying strengths of the solution due to the chemical action alone, or, is the operation of chemical affinity compounded with one or more purely physical forces; and if so, what is the relative part contributed by each?

Messrs. Gladstone and Tribe point out that there are two currents, or mass movements produced, one a light blue ascending stream of a dilute solution of silver and copper nitrates; the other, a deep blue descending current of copper nitrate containing about three times as much HNO_3 as the main solution. Obviously, the first step in the

investigation should be to bring the fluid against the plate with a uniform velocity. To accomplish this a piece of copper was slightly curved and fastened to an arm which carried it round in a horizontal circle of about one inch radius with a uniform speed of five and a half revolutions per second, which gave therefore a linear velocity of the metal through the liquid of nearly 3 feet per second. The strip was suspended from the arm so as to hang vertically, and the area of its surface was known. The results are given in the appended table in the columns marked 2 and 3. It was at once apparent that the absolute rate of action was much greater than when the metal was stationary as in Messrs. Gladstone and Tribe's method, where the only mass motion of the liquid relatively to the plate was caused by gravitation. An inspection of columns 2 and 6 will show this.

Rotation, Brush, and Centrifugal Experiments.

(The numbers given are for 1 square cm. of acting surface, and for 1 minute of time, in fractions of a milligramme of copper dissolved.)

Rotation.			Brush.		Gravity.		Centrifugal.	
Percentage of $AgNO_3$.	Actual weights.	Weights divided by percentage.	Actual weights.	Weights divided by percentage.	Actual weights.	Weights divided by percentage.	Actual weights.	Weights divided by percentage.
1.	2.	3.	4.	5.	6.	7.	8.	9.
0·075	0·087	1·16	—	—	—	—	—	—
0·15	0·185	1·2	—	—	0·00375	0·025	0·089	0·59
0·225	0·315	1·4	—	—	—	—	0·139	0·61
0·30	0·475	1·58	—	—	0·0125	0·041	0·215	0·71
0·375	0·555	1·48	—	—	—	—	—	—
0·45	0·630	1·40	—	—	0·217	0·048	0·337	0·74
0·60	0·925	1·55	—	—	0·0337	0·056	0·484	0·80
0·90	—	—	—	—	0·0646	0·072	0·732	0·82
1·20	—	—	—	—	—	—	1·084	0·90
0·1	—	—	0·018	0·18	—	—		
0·2	—	—	0·074	0·37	—	—		
0·4	—	—	0·270	0·65	—	—		
0·6	—	—	0·337	0·56	—	—		
0·8	—	—	0·411	0·51	—	—		
1·0	—	—	0·537	0·54	—	—		
1·2	—	—	0·722	0·60	—	—		
1·6	—	—	1·070	0·67	—	—		
2·4	—	—	1·600	0·66	—	—		

Avr. 1·48 (rotation, actual weights)

Avr. 0·60. (brush, weights divided by percentage)

Law. Percentages of silver in powers of 2. Copper dissolved will be in the corresponding powers of 2·25.

In column 3 are given the quotients of the actual weights divided by the percentages of silver nitrate. It is apparent that these

numbers tend toward a constant, and in this respect they show a marked contrast to the numbers in column 7.

The experiments were next varied by varnishing the copper on its convex side and holding it rigidly against the side of a beaker while its bare concave face was constantly swept by a rotating cylindrical brush, driven at uniform speed by clockwork. The results are given in columns 4 and 5 where, to secure a greater range for comparison a different order of percentages was employed; and it is evident from column 5 that the absolute rate is less than for the rotation experiments, but is still much greater than for the gravitative record; it is apparent, moreover, that the quotients here also tend to approach a constant.

The first two numbers in columns 3 and 5 depart widely from the others. This is due, I believe, to the necessity of removing the silver each time the copper was weighed, to determine how much of it had been dissolved. When the solution is very weak, the silver crystals are so minute that it is practically impossible to remove them completely, whilst this is not the case with the larger crystals made by stronger solutions.

Now when the extreme difficulties are considered of securing absolutely uniform rotation, of detaching the copper at a given instant, and of preventing accidental cross-currents, these numbers show (since they are the means of many trials) that the chemical action varies directly with the quantity of salt in solution, when the supply of fresh liquid to the surface of the plate is constant and independent of its strength. Within the limits of these experiments, the following law would appear to be true. *In metallic precipitations of dilute solutions, the chemical action varies directly as the mass,* i.e., *percentage of the dissolved salt.*

The experimental work of Messrs. Gladstone and Tribe is above criticism. I made many determinations by their method, with the sole result of confirming their entire accuracy. How then can their law be reconciled with the above statement? The explanation which I venture to offer is the following:—

When the plate is suspended in the liquid, a film of copper nitrate is at once formed against it. Now the access of fresh silver nitrate depends on the removal of copper nitrate; this film being heavier than the main solution begins to fall (a part also rises) and thus drags in fresh liquid from above to attack the copper. The rate at which it falls depends on its density, that is, on the quantity of copper dissolved, but it is resisted by the inertia of the surrounding fluid which it must displace.

Now in a second experiment let the percentage of silver nitrate be doubled, then by the statement made above, the quantity of copper

dissolved in a very small portion of time will also be doubled and its density will be greater. The increase of density may be found from the tables of specific gravities of copper nitrate solutions. Storer's dictionary of solubilities gives the following:—

Percentages of salts.	Densities.
1	1·0059
2	1·0119
3	1·0192
4	1·0252
&c.	&c.

We see that the increment of the density rises a little more rapidly than the increase of the salt, so that the density of a 4 per cent. solution, for example, is 2·11 times that of a 2 per cent. solution. Therefore, the film of copper nitrate will be more than twice as dense when the percentage of silver nitrate is doubled. The rate of motion of the film will, however, not be twice as great; for bodies moving with slow velocity through a liquid are found to experience resistances which vary as the square of the velocity. The density of the film has become more than twice as great, consequently the attraction between it and the earth has more than doubled. It is also evident that although the sp. gr. of the silver salt is increased, yet the increment of the density of the copper solution over that of the silver solution will be more than doubled. Hence its velocity will become not 2, but as the square root of 2, which is 1·41: but as the relative density (or the relative increment) is really more than 2, its square root will approach near to 1·5. The observed rate of action will be composed therefore of the two rates, viz., twice the chemical action because of chemism, multiplied by $1\frac{1}{2}$ because of gravitative action; or, when the percentage of silver salt is doubled, the quantity of copper dissolved will be tripled. But this is Gladstone and Tribe's law.

The above hypothesis leads to this conclusion. If the "2-3 law" is composed of two factors, one of which is chemical action and the other gravitation, then if another accelerating force could be substituted for gravitation, the law ought to change its form, if that force could be made a large one, for the rate of movement of a body through water is determined by resistances which increase much faster than the square of the velocity when the latter is no longer small. Accordingly, I mounted the precipitating vessel on an arm which permitted the whole to revolve in a vertical plane and with a velocity which gives a centrifugal force 30 times greater than the value of the acceleration of gravity. With this large force it was certain that the currents ought to increase much more slowly than in

the ratio of the square root of 2. An inspection of columns 8 and 9 will show the results.

In column 9 the numbers do not tend to approach a constant, but slowly increase. They resemble in this respect the gravitation numbers in column 7, only their rate of increase is slower, as it should be by theory. A mathematical analysis of these numbers, taking the 30 per cent. one as a basis, agrees very closely with those calculated by the formula that doubling the percentage of silver increases the rate of chemical action to 2·25 instead of to 3.

In conclusion, I think it is probable that the true law of chemical action, where one metal precipitates another, should be that the time during which one atom replaces another in a compound molecule is constant, and hence that the rate of total chemical action varies directly as the mass of the reacting body in solution.

LII.—*On Nitrification.* Part III.

By Robert Warington.

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Five years have elapsed since I last reported to the Society (Trans., 1879, 429) the results of my investigations on the process of nitrification, conducted in the Rothamsted Laboratory. During these five years the investigations have been continued, but have been chiefly confined to an attempt to elucidate the causes which determine the nitric or nitrous character of the final product. This special branch of the inquiry, in spite of much labour, is not yet ripe for publication.

Various results, however, have been obtained from time to time, and these I now propose to lay before the Society.

Before describing the new results obtained at Rothamsted, it will be well to notice the recent work of other investigators in the same field, and also to say a few words on the present position of the theory which ascribes nitrification to the action of a living organism.

I must in the first place refer to the excellent paper by J. Soyka (*Zeitsch. f. Biol.*, 1878, 449), with which, though published previously to my last report, I have only lately made acquaintance. It treats chiefly of the nitrification of urine under various conditions. Soyka's experiments directly support the conclusion of Schloesing and Müntz, that nitrification is due to the action of a living organism.

Two papers have been published by Schloesing and Müntz (*Compt. rend.*, **89**, 891, 1074*) since the date of my last communication. In these papers, the authors describe the character of the organism producing nitrification, which they separated by means of systematic cultivations in a fluid medium: the organism is apparently a micrococcus. They also state the range of temperature to which the action of the organism is limited. The influence of various other conditions is described.

There are a few points of difference between the conclusions arrived at by these French chemists and those which I have already published. The first is apparent only. It was stated in my last paper that "bacteria are incapable of producing nitrification." This statement was far too general. It is, in fact, now shown that the nitrifying organism is a member of the great family of bacteria. In the sense, however, in which the phrase was employed it was correct. It was, in fact, used in reference to results showing that nitrification did not commence in solutions largely infected with ordinary atmospheric bacteria, a result with which the later statements of Schloesing and Müntz entirely agree. The second point of difference concerns the temperature at which nitrification ceases. Schloesing and Müntz found 37° to be the most favourable temperature. Nitrification occurred, though at a greatly diminished rate, at 45°, and to a very slight extent at 50°. In my own experiments, already published, I was unable to obtain nitrification at 40°. It is probable that the different result is owing to the different conditions which obtained in the two series of experiments. Unfortunately the methods of work adopted by the French chemists have never been published. The third point of difference is regarding the conditions which determine the formation of nitrites rather than of nitrates in a nitrifying solution. Schloesing and Müntz regard the difference in the product as due to differences

* Some fuller details are given in the *Leçons de Chimie Agricole professées par Th. Schloesing*, 1883.

in the conditions of temperature and aëration. Without denying the influence of certain external conditions, my own results clearly point to a difference in the character of the organism as being in many cases the chief determining factor. It is indeed possible to have two similar solutions, under identical external conditions, in one of which only nitrites, and in the other only nitrates are being produced; the difference being determined by the character of the organisms with which the respective solutions have been seeded.

The late Dr. Angus Smith, in his Report made in 1882 to the Local Government Board, as Inspector under the Rivers' Pollution Prevention Act, has described many experiments on nitrification. While speaking most courteously of the results published by other investigators, leading to the conclusion that nitrification is the work of a living organism, he maintains that nitrification may also take place by a process of simple oxidation by atmospheric oxygen. He says, for instance, on p. 26, "Bodies containing protein compounds, when in abundance of water and in common air, may oxidise and form nitric acid." As this view seems still to be held by others, it will be well to consider briefly the evidence which is adduced.

Dr. Angus Smith's experiments show (as was already known) that ammonia is readily converted into nitrate both by hydrogen peroxide, and by potassium permanganate in the presence of free alkali. They also show that nitrates are abundantly formed when a weak solution of blood is left in contact with permanganate. These results clearly furnish no argument in favour of the view that nitrates may be formed by simple contact with atmospheric oxygen. Dr. Angus Smith further describes experiments in which nitrates were formed in a dilute solution of blood without the addition of other matter. Here we should certainly have evidence of nitrification by simple oxidation, if only precautions had been taken to eliminate the influence of living organisms by a preliminary boiling of the solutions, and their subsequent protection from access of life. Of such precautions, however, there is no mention, and it becomes impossible therefore to attach any weight to the evidence. In my own earlier experiments, unsterilised solutions of ammonium salts, containing the usual nutritive ingredients, were found to nitrify (Trans., 1879, 440); but no nitrification has been observed in solutions sterilised by heat, and afterwards protected from the entrance of organisms. Instances of this will be presently given.

Pichard has recently published experiments (*Ann. Agronomiques*, 1884, 302) on the nitrification of ammonium sulphate, and of earth-nut-cake, mixed with a relatively small proportion of sand, various salts being added, each mass in most cases intentionally receiving a certain quantity of ordinary soil. He concludes that ammonium salts undergo

a partial nitrification by simple exposure to air. Nothing is said, however, about the sterilisation of the sand and calcium carbonate with which the ammonium salt was mixed; the moist sand was indeed placed on a layer of earth, and the air having access was, apparently, unfiltered!

In experiments of this nature, it must always be borne in mind that moist substances, or liquids, exposed to air for a long time, may acquire distinct traces of nitrous acid by mere absorption of the nitrites present in the atmosphere, no nitrification of the substance under investigation having really taken place (Trans., 1881, 229).

During the present year, C. F. A. Tuxen has published (*Tidsskrift for Landökonomie*, 1884) the results of experiments on nitrification, in which different nitrogenous manures were mixed in relatively large quantities with a clay and with a sandy soil, and the course of change studied for more than a year. In a later section, reference will be made to some of his results.

Before discussing the present position of the theory of nitrification, it may be well to describe a few unpublished results which supply evidence on the question.

Some additional Proofs that Nitrification is determined by an Organism.

One important proof that nitrification is determined by the action of an organism is furnished by the fact that the process can be started at pleasure in any suitable solution by adding to the liquid a small quantity of a solution lately nitrified. For this proof to be effective, it must, of course, be shown that without such addition no nitrification will occur. As in the former report, the investigation was still too young for it to be possible to speak of solutions long preserved without nitrification, some examples of this fact will now be given.

On August 11, 1878, two bottles, containing an ammoniacal mixture sterilised by heat, were left unseeded, one having the neck plugged with cotton-wool, the other with the mouth simply covered with muslin. The solutions are particularly described in the Sixth Series of Experiments in the last Report. In duplicate solutions, which had been seeded, nitrification was practically completed by November 4. The unseeded bottle closed with cotton-wool was examined in April, 1879, July, 1880, and August, 1881; at the last date nitrification had not taken place, although three years had elapsed since the solution was prepared. The solution simply protected by muslin was found unnitrified in April, 1879, but nitrification afterwards occurred.

In the present paper, experiments are described (p. 650) in which solutions containing various nitrogenous substances were preserved

for more than a year without nitrification occurring, the seeded duplicates being all nitrified.

It may occasionally happen, from some condition of the experiment, that a solution with which the process of seeding has been gone through is not really seeded, no living nitrifying organism having been introduced; the solution in such a case remains unnitrified, and affords testimony similar to that given by solutions intentionally unseeded. Thus two solutions were seeded in June, 1881, with a nitrified solution which had in one case been previously long exposed to bright sunlight, and in the other had been kept for two hours at 50°; in neither case did nitrification occur, although the subsequent examination of the solutions extended over 19 months. Of 15 solutions seeded with only $\frac{1}{100}$ of a drop of a weak nitrified solution, 9 have remained unchanged. Of 20 solutions seeded with clay subsoil, 17 have not nitrified (see p. 646). This list of illustrations might easily be extended, but the above examples seem sufficient.

We pass next to a new line of proof. If nitrification is due to the vital activity of an organism, it is clear that it can only occur when all the substances necessary for the nutrition of that organism are present. One substance indispensable to all life is phosphoric acid. The following experiments were made as to the effect of leaving out phosphoric acid from the usual nitrifying media. On October 8, 1883, three cultivations were started in the usual ammoniacal mixture; the potassium phosphate being omitted in two cases. All three solutions were seeded with a few drops from a lately nitrified solution. On October 22, nitrification had commenced in the solution containing phosphate, and by November 10 the nitrification of the ammonia was completed. The bottles not supplied with phosphate were examined up to the following June, but in neither case did nitrification take place. It would appear therefore that the presence of phosphates is an essential condition for nitrification, and in this fact we have a further corroboration of the theory which ascribes nitrification to the action of a living organism.

Present Position of the Theory that Nitrification is due to a living Organism.

The evidence in favour of this theory of nitrification appears now to be very complete. Nitrification in soils and waters is found to be strictly limited to the range of temperature to which the vital activity of low organisms is confined. Nitrification is also dependent on the presence of plant-food suitable to organisms of low character. Further proof is afforded by the fact that antiseptics are fatal to nitrification. The action of heat is equally confirmatory. By raising sewage or soil to the temperature of boiling water, its

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nitrifying power is entirely destroyed. Finally, nitrification can be started in boiled sewage, or in other sterilised liquids of suitable composition, by the addition of a few particles of surface soil, or a few drops of a solution which has lately nitrified; while if no such addition is made, these liquids may be freely exposed to filtered air without nitrification taking place.

It is difficult to conceive how the evidence in favour of the ferment theory of nitrification could be further strengthened. Although, however, the greater part of this evidence has been before the scientific public for more than seven years, the theory that nitrification is due to an organism can hardly be said to have obtained any general acceptance; it has not, indeed, been seriously controverted, but neither has it been embraced. It is surely incumbent on those who discuss sanitary and agricultural questions either to accept the theory, and henceforth regard the oxidation of nitrogenous organic matter as effected solely by living organisms, and confined to the conditions suitable for their activity, or to adduce some evidence that nitrification may take place in soils and waters by simple contact with oxygen, when all organisms have been absolutely excluded. Schloesing has apparently given a final blow to the theory that air exists in a condensed state in the pores of a soil, and may on that account exert special oxidising powers, by his recent experiments (*Ann. de la Science Agronomique*, 1884, 1), showing that the gases in a vegetable soil simply occupy the normal volume due to temperature and atmospheric pressure.

Mode of Work in Recent Rothamsted Experiments.

It will be convenient to describe briefly the general mode of work adopted in my own experiments before mentioning the results obtained.

The results to be described have all been obtained by experiments in a fluid medium. The solution most generally employed contained in 1 litre—

Ammonium chloride	80	milligrams.
Sodium potassium tartrate	80	,,
Potassium phosphate	40	,,
Magnesium sulphate.....	20	,,

To this solution, calcium carbonate was generally added to supply the necessary base. When calcium carbonate was not used, 50 mgrms. of gypsum per litre, or in some cases a little tricalcium phosphate, was added. It is necessary to dissolve the magnesium salt separately, and add it to the other ingredients after they have been largely diluted, or precipitation may occur.

Considerable use has also been made of diluted urine, usually of the

strength of 4 c.c. per litre; such a solution has the advantage of simplicity of preparation, but as its strength varies at different times, it is not suitable for standard or comparative experiments.

In special experiments, solutions of various compositions have been employed.

The greater number of experiments have been conducted in short wide-mouthed bottles. The volume of the solution at starting has been 100 c.c., or rather more; the depth of liquid $1\frac{1}{2}$ to 2 inches. The depth has been the same in all comparative experiments.

The bottle containing the solution has its neck closed by a plug of cotton-wool, which is protected from dust by a cap of filter-paper tied over it. Air has thus free access to the solution. The bottle with the solution thus protected is placed in a water-oven, and kept near the temperature of boiling water for six or eight hours to destroy any organisms present. When cool the solution is ready for use.

The calcium carbonate usually employed to furnish the necessary base is prepared by precipitation, and generally added in a moist state. In the case of urine solutions, the calcium carbonate is added before the sterilisation of the liquid; in the case of solutions of ammonium salt, it is added afterwards, the wet calcium carbonate being in this case freshly boiled before use.

The seed employed to start nitrification in the solutions consists either of a small quantity of fresh soil, usually about 0·1 gram, or more generally of 1 c.c. of a solution already nitrified. The nitrified solution was always shaken before the removal of a portion to serve as seed.

In all the earlier experiments, the cotton-wool plug was lifted out, both during seeding, and during each subsequent removal of the solution for examination. These operations were, however, always conducted in a separate room, kept locked until the arrival of the operator, and great pains were taken to avoid raising any dust. With these precautions it was found, as a rule, that bottles might be safely opened without the introduction of any nitrifying organisms. During the last year and a half, however, the removal of the plug has been discontinued; the plug is now simply raised, and the end of a pipette, drawn out to capillary dimensions, is introduced between the plug and the side of the neck; in this way liquids may be introduced or removed at pleasure. When a portion of the liquid is being removed by suction, some cotton-wool is pressed round the tube of the pipette, so that only filtered air may gain admission to the bottle. These precautions are adopted from Klein's method. In both the earlier and later experiments, the pipette was kept immersed in boiling water till the instant it was required for use; after use it was washed, and again replaced in the boiling water till next required. For many

experiments, precautions against the entrance of nitrifying organisms were quite unnecessary, but the method described was still generally employed with the object of keeping the solutions free from moulds and other foreign growths.

The bottles, after seeding, were usually placed in a dark cupboard,* and exposed to the ordinary temperature of the laboratory, which was warmed by a stove in winter time. When the cultivation was to proceed at a higher temperature, the bottles were placed in a covered metal box, having a water-jacket, the temperature of which was maintained at the desired point by means of Page's gas-regulator.

The commencement of nitrification in a solution was determined by testing with diphenylamine. 1 c.c. of the solution was placed in a very small beaker, a drop of solution of diphenylamine sulphate in sulphuric acid added, and then 2 c.c. of concentrated sulphuric acid, and mixture effected by agitation; the development of a violet-blue colour shows the presence of nitric or nitrous acid. This test will detect 1 part of nitric nitrogen in 20,000,000 of water.

The subsequent course of the nitrification was ascertained by repeated examinations for ammonia by Nessler's reagent, and for nitrous acid with metaphenylenediamine; each experiment was made with 5 c.c. of the solution, and the test-tubes employed were always of the same size. The reactions obtained were recorded as "trace," "small," "moderate," "considerable," "large," or "abundant." If the change were to nitrites only, the ammonia would fall from "large" to "trace," while the nitrous acid increased from "trace" to "large;" if the change were to nitrates only, the ammonia would diminish without any corresponding production of nitrous acid. It must be recollected, however, that in solutions kept at a high temperature, and in the case of solutions at ordinary temperatures if the ammonia was present as carbonate, the ammonia may gradually disappear without any corresponding production of nitrates or nitrites, if the bottle is not stoppered but merely closed with cotton-wool. Working in the manner now described, with solutions always containing the same proportion of ammonium chloride at starting, a good idea was generally obtained of the course of the nitrification. The disappearance of all ammonia marked the completion of the process. This method of examination was adopted with the special object of studying the effect of various conditions on the nitric or nitrous character of the change, a subject with which we are not at present concerned; it

* The paper by Messrs. Downs and Blunt, showing the prejudicial influence of light on the development of bacteria, was read at the Royal Society on the same evening that my own communication, mentioning the same fact with regard to the nitrifying organism, was made to the Chemical Society. In Soyka's experiments the prejudicial effect of light on nitrification is plainly shown.

equally served, however, to fix in every case the commencement and termination of nitrification. In some few cases, quantitative determinations of nitrous and nitric acid were made.

The Distribution of the Nitrifying Organism in the Soil.

That the special organism which nitrifies ammonia exists in abundance in the surface soil of all fertile land may be considered as now established by a variety of evidence; it appeared of considerable interest to ascertain to what depth in the soil its presence extended.

In the autumn of 1883, samples of soil were taken for analysis from various depths in the experimental Rotation Field (Agdell) at Rothamsted; the sampling of the soil extended to the depth of 9 feet. The pits formed for this purpose were turned to account for the present inquiry. The surface soil in this field (that which is annually turned by the plough) is about 6 or 7 inches deep, and of a grey colour when moist. Beneath this, with often a sharply defined boundary, comes a reddish-yellow clay containing many flints. Into this clay the deeper root and worm-holes pass, the former often extending 4 feet or more. The former course of a root is indicated by a dark streak in a section of the clay, and by the bleaching of the clay in the immediate vicinity. Below the clay subsoil comes chalk, but this was not reached in the samples of soil with which we are at present concerned.

On November 17, 1883, a series of samples of soil and subsoil were taken from the pit on Plot 1;* the samples being taken from a depth of 2 inches, 9 inches, 18 inches, 3 feet, 6 feet, and 8 feet from the surface; the samples from the lowest three depths were taken in duplicate. The samples of subsoil were taken from the solid clay, all channels being avoided. A fresh surface was first cut on the side of the pit at the spot selected for sampling; this surface was scraped with a freshly ignited platinum spatula; then, the spatula having been washed, re-ignited, and cooled, a portion of soil was detached by the spatula and at once transferred into one of the usual bottles containing a sterilised urine solution of the strength of 4 c.c. per litre; each bottle contained some precipitated calcium carbonate. The quantity of soil taken varied of course; it was about 0·1 gram. It is obvious that as the cotton-wool stopper had to be lifted to introduce the soil, opportunity was given for the entrance of any organisms floating in the air. Experience, however, has shown that air free from soil dust very seldom contains nitrifying organisms, and this

* The rotation on this Plot is—turnips, barley, bare fallow, wheat. The turnips receive a liberal nitrogenous and cinereal manuring, and are fed on the land. The soil samples were taken after the wheat crop.

view is confirmed by the results of the present experiments. The seeded bottles were placed in a dark cupboard of moderate temperature.

On December 15, 1883, an exactly similar series of samples was taken from a pit dug in Plot 8 in the same field,* the whole operation being conducted precisely as before.

The two series of urine solutions thus seeded with soil and subsoil were examined from time to time to ascertain when nitrification commenced, and when this had happened the approximate date of its completion. The results of these examinations are given in the following tables. The completion of nitrification is indicated by a small vertical line.

Nitric or Nitrous Acid produced in Dilute Urine, seeded with Clay Soil (Agdell Field, Plot 1) from various depths, on November 17, 1883.

Depth from which Soil taken.	Jan. 30 (74 days).	March 8 (111 days).	May 6 (170 days).	June 14 (209 days).	July 22 (247 days).	Sept. 17 (304 days).	Oct. 18 (335 days).
2 inches....	large |	—	—	—	—	—	—
9 „	none	none	trace	large |	—	—	—
18 „	„	considerable	large |	—	—	—	—
3 feet (A) ..	„	none	none	none	none	none	none
„ (B) ..	„	„	„	„	„	„	„
6 „ (A) ..	„	„	„	„	„	„	„
„ (B) ..	„	„	„	„	„	„	„
8 „ (A) ..	„	„	„	„	„	„	„
„ (B) ..	„	„	„	„	„	„	„

Nitric or Nitrous Acid produced in Dilute Urine, seeded with Clay Soil (Agdell Field, Plot 8) from various depths, on December 15, 1883.

Depth from which Soil taken.	Feb. 18 (65 days).	March 22 (97 days).	May 6 (142 days).	June 14 (181 days).	July 22 (219 days).	Sept. 17 (276 days).	Oct. 18 (307 days).
2 inches....	moderate	large |	—	—	—	—	—
9 „	none	none	none	trace	large |	—	—
18 „	small	large |	—	—	—	—	—
3 feet (A) ..	none	none	none	none	none	moderate	considerable
„ (B) ..	„	„	„	„	„	none	none
6 „ (A) ..	„	„	„	„	„	„	„
„ (B) ..	„	„	„	„	„	„	„
8 „ (A) ..	„	„	„	„	„	„	„
„ (B) ..	„	„	„	„	„	„	„

* The rotation on this Plot is—turnips, barley, beans or clover, and wheat. The turnips receive a liberal nitrogenous and cinereal manuring, and are carted off the land. The soil samples were taken after the wheat crop, which followed clover.

When examined on January 30, 1884, the solution seeded with soil from Plot 1, 2 inches from the surface, was found to be completely nitrified. The other solutions seeded with soil 2 inches, 9 inches, and 18 inches from the surface nitrified after a longer period, and in the case of the soil taken at 9 inches from the surface the commencement of nitrification was greatly delayed. It may be assumed that long delay in the commencement of nitrification (with favourable external conditions) implies the presence of a very minute quantity of organism in the solution, or that this organism is of exceptionally feeble character.

It will be seen that the subsoils from the depth of 3 feet, 6 feet, and 8 feet did not produce nitrification, except in the case of one bottle out of four receiving subsoil from a depth of 3 feet; in this case, nitrification commenced so extremely late that I am disposed to think it more probable that some nitrifying organism gained access to the solution during its examination on July 22, than that the organism was originally present in the subsoil. The question, however, must remain open to doubt.*

In the above experiments, the nitrifying organism was not certainly found below 18 inches from the surface. A third series of experiments was started on April 5, 1884, with the view of examining in more detail the soil lying within a moderate distance below the surface. In this case, the soil and subsoil were taken from a pit dug at the north end of Agdell Field.† Samples were taken from 3 inches, 6 inches, 9 inches, 15 inches, 2 feet and 3 feet from the surface; the experiments with soil from the last four depths were made in duplicate. All the operations were conducted precisely as before. The results yielded by the subsequent examinations of the solutions were as follows:—

* If the nitrifying organism was actually furnished by the soil, its period of incubation was more than 219 days; this would be far longer than has occurred in any other experiment. In dilute cold solutions the period of incubation has extended to 50 or 70 days, when the organism supplied has been small in quantity and feeble in character. The longest periods yet noticed are those mentioned in the above experiments with clay subsoil.

† This portion of the field is unmanured; it is cropped with turnips (carted), barley, beans or clover, and wheat. The preceding crop was wheat.

Nitric or Nitrous Acid produced in Dilute Urine, seeded with Clay Soil (Agdell Field, North End) from various depths, on April 5, 1884.

Depth from which Soil taken.	May 26 (51 days).	June 16 (72 days).	July 22 (108 days).	Sept. 1 (149 days).	Oct. 27 (205 days).
3 inches	trace	small	large	—	—
6 „	none	trace	considerable	large	large
9 „ (A) ..	„	none	trace	considerable	large
„ „ (B) ..	„	trace	moderate	considerable	considerable
15 „ (A) ..	„	none	none	none	none
„ „ (B) ..	„	„	„	„	„
2 feet (A)	„	„	„	„	„
„ (B)	„	„	„	„	„
3 „ (A)	„	„	„	„	„
„ (B)	„	„	„	„	„

The urine solution employed in this series of experiments was in reality, though not intentionally, considerably stronger than that used in the two earlier series, the conclusion of nitrification was thus in all cases delayed. The sample of soil taken nearest to the surface was the first to start nitrification in the urine; the samples from 6 inches and 9 inches depth also proved effective. The subsoil from 15 inches downwards failed to produce nitrification. The time allowed for trial was indeed shorter than in the two preceding series, but it included the whole of an exceptionally warm summer, when the temperature was especially favourable for nitrification. The results of this latter series of experiments thus show a more limited distribution of the nitrifying organism in the subsoil than that indicated by the earlier series; there soil taken from a depth of 18 inches proved effective, here soil from a depth of 15 inches fails.

The three series of results just described may be thus summarised: In four experiments made with soil 2, 3, and 6 inches from the surface, and four experiments with soil 9 inches from the surface, there was not one case of failure in the production of nitrification. With soil below 9 inches the result was irregular. Out of twenty experiments, nitrification has occurred in three instances only, namely, in two instances with soil from 18 inches, and in one instance with soil 3 feet from the surface; these results appear exceptional, as in two experiments with soil 15 inches from the surface no nitrification was produced, neither did any occur in two experiments with soil 2 feet, and in five experiments with soil 3 feet from the surface. There is also some probability that the nitrification occurring with soil 3 feet from the surface was really due to some accidental contamination, as

the solution remained for 219 days without any appearance of nitrification, which occurred only after a still longer period.

I am disposed to conclude that in our clay soils the nitrifying organism is not uniformly distributed much below 9 inches from the surface. On much slighter grounds it may perhaps be assumed that the organism is sparsely distributed down to 18 inches, or possibly somewhat further. At depths from 2 feet to 8 feet there is no trustworthy evidence to show that the clay contains the nitrifying organism. It is however probable that the organism may occur in the natural channels which penetrate the subsoil at a greater depth than in the solid clay. In the case of sandy soils, we may probably assume that the organism will be found at a lower depth than in clay.

The only published researches I am aware of on the presence of the nitrifying organism in the subsoil, are those made by Müntz and Aubin with portions of rock taken near the summit of the Pic du Midi, 2877 metres above the sea level (*Annales de l'Institut National Agronomique*. Paris, 1883). A disintegrating schistous rock was blasted with gunpowder; a sample of rock taken more than 50 centims. from the surface produced a feeble nitrification when introduced into a sterilised medium.

The distribution of bacteria in soil has been made the subject of microscopical investigation by Koch (*Jahresb. d. Agricultur Chemie*, 1881, 43). He states that the micro-organisms in the soils he has examined diminish rapidly in number with an increasing depth, and that at the depth of scarcely a metre the soil is nearly free from bacteria. Pumpelly and Smyth (*Annual Report of the National Board of Health*, 1883) have made some experiments with soil carefully removed from the side of a well newly dug in a hard blue clay. In four experiments, clay 1 foot, 2 feet, and 6 feet from the surface, produced infection in a sterilised solution, while clay 9 feet from the surface was without effect. It is of course probable that those organisms which do not require a considerable supply of oxygen to exercise their functions will be able to exist at lower depths in the soil than the nitrifying bacterium.

Some important practical conclusions seem to follow from the limitation of the nitrifying organism to the upper layer of the soil. Thus it is evident that the oxidation of nitrogenous matter in soil will be confined to matter near the surface. The nitrates found in the subsoil, or in the subsoil drainage waters, have really been produced in the surface soil, and have passed down by diffusion, or in a descending column of water. Again, in arranging a filter-bed for the oxidation of sewage, it is obvious that when dealing with a heavy soil lying in its natural state of consolidation very little will be gained by

making the filter-bed of considerable depth. If, on the other hand, an artificial bed is to be constructed, it is clearly the top soil, rich in oxidising organisms, which should be exclusively employed.

Nitrogenous Substances susceptible of Nitrification.

The laboratory experiments described in the previous reports were made either with soil, or with solutions containing ammonia. Since then many experiments have been made with diluted urine as the nitrifying medium. Successful trials have also been made on the nitrification of solutions of asparagine, milk, and rape-cake. Thus, besides ammonia, two amides, and albuminoïds in two forms, have proved susceptible of nitrification. The details of the last-named experiments were as follows. It will be observed that each series included experiments on the behaviour of the solution when left unseeded by the nitrifying organism.

Urine and Milk Solutions.—A solution of urine (3 c.c. per litre) was placed in three bottles. At the same time a solution of new milk (4 c.c. per litre) was also placed in three bottles. In every case, the liquid was 2 inches in depth. The bottles were closed with cotton wool, and heated in boiling water for one hour. To two bottles in each series calcium carbonate was added, and one of the solutions so treated was seeded on July 8, 1882, from a freshly nitrified solution. The seeded urine solution was examined on September 4; nitrification was then completed. The seeded milk solution was examined on September 25; a large amount of nitric acid, but no ammonia, was then present. A subsequent quantitative determination by Schloesing's method showed the presence of 18·1 parts of nitric nitrogen per million in the milk solution. The four unseeded solutions of urine and milk were examined for nitric and nitrous acid on August 20, 1883, nearly 14 months after the solutions were prepared; none was found in the milk, a trace only in the urine.* Since these experiments were made, diluted milk has frequently been nitrified in the laboratory; ammonia is always formed as a preliminary stage of the process.

Asparagine Solutions.—The asparagine solution was prepared on September 23, 1882; it contained, per litre, 107 mgrms. asparagine (dried over sulphuric acid), 80 mgrms. sodium potassium tartrate, 40 mgrms. potassium phosphate, and 20 mgrms. magnesium sulphate. The solution was placed in four bottles, to each of which calcium carbonate was added. The depth of liquid and mode of sterilising were the same as in the preceding experiments. Three of the

* Information as to the presence of nitric acid in fresh urine will be found on page 669.

solutions were seeded from freshly nitrified liquids. On October 2, one of the seeded solutions was tested, and a considerable amount of ammonia found; the sterilised unseeded liquid had shown only a trace of ammonia with Nessler's reagent. On October 23, nitrification was apparently completed in all the seeded solutions. The nitrification of the asparagine solution was exceptionally speedy; the formation of ammonia apparently preceded that of nitric acid. In October of the following year, a quantitative determination of nitric acid, made in a mixture of the seeded solutions, showed 26·1 parts of nitric nitrogen per million; the solutions had evidently concentrated by keeping. The unseeded solution when opened 12 months after its preparation contained only a trace of ammonia; no nitrification had occurred.

Rape-cake Solutions.—An extract of the cake in cold water was filtered, made slightly alkaline with sodium carbonate, boiled, and again filtered. As the amount of nitrogenous matter in the solution was unknown, it was divided into two portions, one, half as concentrated as the other. The bottles containing the solutions received calcium carbonate, and in other respects were treated as above described. One solution of each strength was seeded on October 14, 1882; one solution of the weaker strength remaining unseeded. The solutions then contained only a trace of ammonia. On November 20, ammonia was present in some quantity in both the seeded solutions, but no nitric or nitrous acid. On December 18, the ammonia had still further increased. On January 30, 1883, a trace of nitrous or nitric acid was found by diphenylamine in the weaker solution, none in the stronger. On February 19 nitrification had made scarcely any progress. More calcium carbonate was now added, and both bottles placed in an air-bath kept at 20°. On March 13, as the stronger rape-cake solution had not begun to nitrify, and but little change had taken place in the weaker solution, both were re-seeded with 1 c.c. of a recently nitrified solution. From this time nitrification proceeded rapidly. On April 14, nitrification was completed in the weak rape-cake solution, and almost completed in the stronger. In the following October, a quantitative determination of nitric acid was made in the weaker solution by Schloesing's method; it was found to contain 33·2 parts of nitric nitrogen per million. The unseeded rape-cake extract, examined at the same time, was unnitrified. The seeded rape-cake extracts were clearly nitrified with difficulty, some hindrance apparently occurring in the earlier stages of the process.

Evidence of the nitrifiability of rape-cake when applied to land as manure is afforded by the analysis of the drainage waters from the experimental wheat field at Rothamsted. Each plot in this field has a drain-pipe, 2 to 3 feet from the surface, running down the middle of

it. On one plot coarsely powdered rape-cake (1,700 lbs. per acre, 1878 to 1881, 1889 lbs. since 1881) is ploughed in towards the end of October. On 15 occasions during the last six years, the winter drainage waters from the rape-cake plot, and from two unmanured plots, have been simultaneously collected and analysed. The mean amounts of nitric nitrogen in the drainage from the two unmanured plots were respectively 5·3 and 5·1 per million, while in that from the rape-cake plot it amounted to 13·7 per million.

Boussingault nitrified 50 per cent. of the nitrogen of rape-cake when the latter was mixed with soil (*Compt. rend.*, **82**, 477). Pichard, in the experiments already referred to, nitrified 46 per cent. of the nitrogen of earthnut-cake, when the latter was mixed with sand, and seeded with fertile soil. Hatton (Trans., 1881, 264) obtained but little nitric acid by filtering a solution of rape-cake during nine days through a column of sand, but he observed a considerable production of ammonia; the action in this experiment was clearly uncompleted.

The question of the production of nitric acid from rape-cake has been gone into in some detail, as it has been denied by some that vegetable substances are susceptible of nitrification. There is surely, however, no scientific ground for supposing that the amides and albuminoïds of plants differ as to their capacity for nitrification from the amides and albuminoïds of the animal body, nor are there any experiments indicating that such a difference exists. It is true that some nitrogenous vegetable substances are not easily nitrifiable, but the same may be said of such animal substances as hair. It is, however, freely admitted that, in a given time, ordinary vegetable tissue will yield far less nitric acid than animal tissue; partly for the obvious reason that it contains less nitrogen, but partly also because the excess of carbonaceous matter in the vegetable tissue has also to be oxidised. The available oxygen is thus, in the case of vegetable tissue, largely consumed in the production of carbonic acid, whilst in the case of animal tissue a much larger proportion is devoted to the oxidation of nitrogen.

Few comparative results have been obtained as to the relative rapidity of nitrification in solutions containing the same amount of nitrogen in various forms. At present, speaking only of very weak solutions provided with the proper nutritive ingredients, I should be disposed to say that nitrification takes place most speedily in solutions of ammonium salts and asparagine, less speedily in urine, and with distinctly more difficulty in solutions of milk and rape-cake.

In all cases in which non-ammoniacal substances were employed, the first stage of the process was the production of ammonia. C. F. A. Tuxen, in a paper already referred to, has published

experiments on the formation of ammonia and nitric acid in soils to which bone-meal, fish-guano, or stable manure had been applied; in all cases he found that the formation of ammonia preceded that of nitric acid. As far therefore as information goes at present, it would seem probable that ammonia is, strictly speaking, the only nitrifiable substance; practically, ammonium carbonate is the material from which nitric acid is in all cases produced. With this idea before us, we may safely assert that all nitrogenous bodies are nitrifiable which yield ammonia when attacked by the organisms present in fertile soils.

Influence of Various Conditions on the Process of Nitrification.

1.—*Alkalinity of the Solution.*

It has been acknowledged by every investigator that the presence of some salifiable base is one of the conditions essential for nitrification. In the last Report (third series) some experiments illustrating this fact were described, and two more recent ones may here be mentioned. On August 25, 1883, six solutions of the composition given at p. 642, save that the sodium potassium tartrate was only 40 mgrms. per litre, were seeded from a freshly nitrified liquid. Two of the solutions received no added base, two received precipitated calcium carbonate, and two a small quantity of sodium carbonate. The six bottles were all placed in the same cupboard. In two of the solutions receiving base, nitrification was completed in 51 days; in the other bottles receiving base, nitrification terminated in 65 days. In the two solutions receiving no base, a small quantity of nitric acid was found at the end of a year, but the ammonia unnitrified was still abundant.

It appeared of some importance, from a practical point of view, to ascertain to what extent nitrification would proceed in the case of diluted urine, without the assistance of an added base. The experiment was made in wide-mouthed pint bottles provided with cotton-wool stoppers; 320 c.c. of diluted urine (4 c.c. per litre) were placed in each bottle, forming a column $3\frac{5}{8}$ inches deep. The series was as follows:—

U, containing diluted urine alone.
UCa, containing diluted urine with $CaCO_3$.
UCaNa, containing diluted urine with $CaCO_3$ and Na_2CO_3.
UG, containing diluted urine with glucose.
UGCa, containing diluted urine with glucose and $CaCO_3$.
UGCaNa, containing diluted urine with glucose and $CaCO_3$ and Na_2CO_3.

The proportion of glucose was 100 mgrms. per litre, of sodium carbonate 250 mgrms. All the bottles were seeded on May 1, 1882, with 1 c.c. of a solution recently nitrified by soil.

On June 19, no nitrous acid was present in U, and in UG a trace only; in the other solutions containing an added base, a distinct, and in some cases considerable amount was found.

On July 8, only a very small quantity of ammonia remained in UCa, UCaNa, and UGCaNa; the quantity was considerable in UGCa, and very considerable in U and UG.

On August 7, the ammonia had disappeared from UGCa, it was still considerable in the case of U and UG.

On September 4, nitrous acid having disappeared from the solutions, some quantitative determinations of nitric nitrogen were made by means of indigo; the results were as follows:—

Solution U,	9·7	of nitric	nitrogen	per million.
„ UCa,	25·6	„	„	„
„ UCaNa,	23·1	„	„	„

The solutions were left undisturbed till October 3 in the following year. The quantity of ammonia was then still considerable in the case of U and UG. Quantitative determinations were again made, this time by the more exact method of Schloesing. The results were as follows:—

Solution U,	12·8	of nitric	nitrogen	per million.
„ UG,	12·7	„	„	„
„ UCa,	25·9	„	„	„

Thus 17 months after the seeding of the urine solutions, and 14 months after nitrification had ceased in all the solutions supplied with a base, the nitrogen of the urine solutions not so assisted was only one-half nitrified. The reason of this result is not far to seek. The first stage in the nitrification of urine is undoubtedly the conversion of the urea into ammonium carbonate; this, of course, plays the part of a base, and nitrification may proceed vigorously till the whole of the ammonium carbonate is converted into ammonium nitrate (or nitrite); at this point the action must stop, unless some other base is available. We should infer therefore, on theoretical grounds, that in the absence of any additional base, only one-half of the nitrogen contained in a solution of ammonium carbonate would be nitrifiable, and this is precisely the limit of nitrification which has appeared in the diluted urine experimented with.

The practical bearing of the fact thus established is obvious. Neither urine, nor sewage containing it, necessarily includes within itself the constituents requisite for complete nitrification. Nor will

intermittent filtration through soil necessarily affect a complete oxidation of ammonia. For nitrification to be complete, there must always be present in the sewage, or in the soil through which it is filtered, a sufficient quantity of easily salifiable base to combine with the nitric acid produced. If the supply of base is insufficient, nitrification will be incomplete. If no additional base be present, nitrification can at most extend to only one-half of the ammonia, and will often fall short of this, as only in certain cases will the whole of the ammonia exist as carbonate.

In the course of the general investigation, cultivations have been made under various conditions, both as to the amount and character of the base present. In most of the experiments, precipitated calcium carbonate in excess was added to the solution, and has furnished practically the whole of the base required for nitrification. When calcium carbonate is added to a cold solution of ammonium chloride, the alkalinity of the liquid is of course very feeble, the conditions only admitting the formation of a very small proportion of ammonium carbonate. In other experiments, varying proportions of disodium carbonate, monosodium carbonate, or of the carbonates of ammonium, have been employed; in all these cases, the alkalinity of the liquid has been more or less increased.

It appears from the results at command, that the addition of a small proportion of disodium carbonate, Na_2CO_3, to an ammonium chloride solution containing calcium carbonate, increases the speed of nitrification; whilst a larger proportion retards the process, or may prevent nitrification altogether.

In seven pairs of experiments made at various times, the period required for nitrification in a solution supplied only with calcium carbonate was compared with that required in a similar solution containing in addition 160—200 mgrms. of disodium carbonate per litre.* In four instances, nitrification was considerably more speedy where the disodium carbonate was present; in two instances, the speed was nearly alike in the comparative experiments; in one instance (a shallow solution), nitrification took place more speedily without sodium carbonate. The presence of the disodium carbonate was thus, on the whole, an advantage.

In sixteen instances, in which the effect of calcium carbonate, used alone, was compared with that of 320 mgrms. of disodium carbonate

* Nearly all the experiments on the comparative influence of calcium carbonate, disodium, and monosodium carbonate, were made with the ordinary solution containing 80 mgrms. of ammonium chloride per litre. In such a solution, 160 mgrms. of disodium carbonate will almost exactly suffice to combine both with the chlorine and with the nitric acid produced. The solution at the end of the operation would thus be nearly neutral.

per litre, also used alone, nitrification was in 13 instances distinctly less speedy with the sodium than with the calcium carbonate, whilst in 3 instances the progress was nearly alike under both conditions.

In five comparisons between the effect of calcium carbonate, and 480 mgrms. of disodium carbonate per litre, used alone, all the solutions receiving calcium carbonate nitrified long before those receiving sodium carbonate; in fact, nitrification did not take place in three of the latter.

From these comparisons, it would appear that in an ammonium chloride solution, with the conditions described, an alkalinity equal to 160—200 mgrms. of disodium carbonate per litre is on the whole favourable to nitrification, whilst an alkalinity of 320 mgrms., or more, is unfavourable.

To ascertain more completely the influence of different degrees of alkalinity, and also the comparative effect of different alkaline substances, the following series of experiments was made.

The chloride of ammonium solution employed was of the usual composition, save that it contained only 40 mgrms. of sodium potassium tartrate, and 50 mgrms. of gypsum per litre. 100 c.c. of this solution were placed in each of 15 bottles. To five of these, disodium carbonate was added, in the proportions 1, 2, 4, 6, 8, the unit taken being 160 mgrms. per litre. To five, monosodium carbonate (NaH_2CO_3) was added in such quantity as to equal the disodium carbonate in alkalinity. To the remaining five bottles, ammonium carbonate (white outside crust of lumps) was added in similar quantity and proportion. The ammonium carbonate solutions were placed in stoppered bottles, the others in bottles having cotton-wool stoppers. All the solutions received a liberal seeding on February 25, 1884. The results of the subsequent examinations for nitrous and nitric acids are given in the following table (p. 657). The entire disappearance of the ammonia is indicated, as before, by a vertical line.

According to the table, the solutions containing 1 and 2 units of disodium carbonate (160 and 320 mgrms. per litre) nitrified at the same rate; in fact, however, the less alkaline solution was always somewhat ahead, though not to such an extent as to require the use of different terms in the table. With 4 units of disodium carbonate (640 mgrms. per litre), the commencement of nitrification was delayed about 26 days. With 6 and 8 units of disodium carbonate (960 and 1280 mgrms. per litre), nitrification was certainly delayed from 90 to 100 days, and it is even doubtful whether nitrification took place at all in the case of the stronger solution. Several practical difficulties occur in experiments conducted in the above manner. If the trial is prolonged, and the temperature that of summer, the ammonia is volatilised through the cotton-wool stopper; the alkali-

Nitric or Nitrous Acid produced in Ammoniacal Solutions under different conditions of Alkalinity, seeded February 25th, 1884.

Proportion of Alkaline Salt present.	Mar. 22 (26 days).	April 17 (52 days).	May 7 (72 days).	May 24 (89 days).	July 7 (133 days).	Sept. 6 (194 days).
	Disodium Carbonate Series.					
1.	trace	moderate	large	—	—	—
2.	trace	moderate	large	—	—	—
4.	none	trace	moderate	considerable	—	—
6.	,,	none	none	none*	small	small
8.	,,	,,	,,	,, *	trace	,,
	Ammonium Carbonate Series.					
1.	moderate	abundant	—	—	—	—
2.	small	abundant	—	—	—	—
4.	none	none	trace	abundant	—	—
6.	,,	,,	small	abundant	—	—
8.	,,	,,	none	none*	none	none
	Monosodium Carbonate Series.					
1.	small	large	—	—	—	—
2.	,,	,,	—	—	—	—
4.	,,	,,	—	—	—	—
6.	,,	,,	—	—	—	—
8.	trace	considerable	large	—	—	—

nity of the solution is thus reduced below that fixed at starting; and if nitrification occurs at a late period it is prematurely concluded, there being little ammonia left to be nitrified.

In the ammonium carbonate series, we find the order of the commencement of nitrification similar to that observed in the case of the solutions containing disodium carbonate; the weakest solution is here again the first to exhibit nitrification. In this series, an alkalinity of 6 of the adopted units (probably about 260 mgrms. nitrogen per litre at the time of nitrification) is evidently nitrifiable, though slowly; but with an alkalinity of 8 units no certain evidence of nitrification was obtained.

In the monosodium carbonate series, we meet with wholly different results. On the first day of examination, nitrification was found to have commenced in all the solutions; the amount of nitrification was here again inversely in proportion to the alkalinity, but the differences, except in the case of the strongest solution, were too small to affect the terms adopted in the table. Nitrification was soon completed in all the solutions.

* At this date these solutions were again seeded from a nitrified solution.

It appeared from these experiments, that any increase in the alkalinity of the solution was attended with further delay in the commencement of nitrification; that with disodium carbonate a solution containing 960 mgrms. per litre could scarcely be nitrified; that ammonium carbonate presented rather less obstacle, the 6-unit solution (about equal in alkalinity to 960 mgrms. of disodium carbonate) nitrifying with some ease, but no nitrification occurring in a solution of one-third greater strength. Monosodium carbonate, on the other hand, had distinctly less prejudicial effect; and in this case, apparently, the limit of alkalinity at which nitrification ceases was not reached, though about 2050 mgrms. of monosodium carbonate per litre were employed.

As the maximum proportion of monosodium carbonate which may be present in a solution without preventing nitrification had not been ascertained, a further series of experiments was commenced on May 8, 1884. The solution employed was of the same composition as before. To one series of solutions 8, 12, 16, and 20 units of monosodium carbonate were added; and to another series 4, 6, 8, and 10 units of disodium carbonate, prepared by gently igniting the equivalent quantity of monosodium carbonate. The exact comparison of the two carbonates was thus insured.

The experiment was not as successful as could be wished, for during the warm summer months the ammonia almost entirely disappeared from the solutions not yet nitrified. In the solution containing 4 units (640 mgrms. per litre) of disodium carbonate, nitrification commenced in 53 days, but from the cause already mentioned no certain evidence of nitrification was obtained in the more alkaline solutions. In the monocarbonate series, the solution containing 8 units (2100 mgrms. per litre) showed nitrification in 32 days, but no distinct evidence of nitrification was obtained when 12 units were present. The results thus confirmed in great measure those already obtained, but without adding any new facts.

In a third series of experiments, carbonates of ammonium were compared containing different proportions of carbonic acid, this condition evidently having considerable influence on the result in the experiments with sodium carbonates. A solution was employed of the same composition as before, and to it was added ammonium carbonate taken in some cases from the white opaque crust of lumps of commercial carbonate, and in other cases obtained from the clear central mass of such lumps. As the composition of these carbonates was not strictly known, we may designate them for the present purpose as ammonic and ammonious carbonates. The ammonic carbonate was employed in the proportion of 4, 6, 8, and 10 units, the ammonious carbonate in the proportion of 2, 4, 6, and 8 units;

the unit was in all cases based on alkalinity. The experiments were made in rather loosely stoppered bottles. The quantity of ammonia was far too great to disappear entirely by volatilisation in the course of the experiment. The solutions were seeded on May 28, 1884.

The solution with 2 units of ammonious carbonate showed a commencement of nitrification in 36 days, that with 4 units in 71 days; no other solutions in the series nitrified. With ammonium carbonate, the solution with 4 units exhibited nitrification in 36 days, and that with 6 units in 57 days; no others nitrified. At the time of its nitrification, the 4-unit solution of ammonious carbonate exhibited an alkalinity equal to about 140 parts of nitrogen per million; the 6-unit solution of ammonic carbonate an alkalinity equal to about 220 parts of nitrogen per million. The maximum proportion of ammonium carbonate capable of nitrification is here shown to be the same as in the first series of experiments. As in the case of the sodium carbonates, it is further clearly shown that the larger the proportion of carbonic acid united with the base, the less is the prejudicial influence of the salt on nitrification.

Other experiments having shown that, under conditions unfavourable to nitrification, important aid is afforded by increasing the amount of the nitrifying organism present, a fourth series of experiments with ammonium carbonate was commenced, in which 1 gram of fresh arable soil was added to each solution. The solution employed was more concentrated than before; it contained per litre—sodium potassium tartrate, 1·0 gram; potassium phosphate, 0·3 gram; magnesium sulphate, 0·1 gram. The ammonium carbonate (tolerably clear pieces) was used in the proportion of 6, 8, 10, 12, 14, and 16 units. The experiment commenced on July 14, 1884.

In the solution containing 6 units of ammonium carbonate, nitrification commenced after 78 days; its alkalinity was then determined by experiment, and was equivalent to 245 parts of nitrogen per million. The solution containing 8 units of ammonium carbonate commenced to nitrify after 96 days, its alkalinity being then equal to 368 parts of nitrogen per million.* No other solution has at present nitrified, though 129 days have now elapsed since seeding. It will be noticed that under these more favourable conditions a stronger solution of ammonium carbonate was nitrified than in the preceding series.

On comparing the results with ammonium carbonate with those obtained in solutions containing sodium carbonate, it appears that nitrification is possible with an alkalinity equal to 368 parts of nitrogen (as ammonia) per million in the case of ammonium carbonate,

* This alkalinity is somewhat above that of the ammonium carbonate added (N = 344 per million): additional alkali had probably been derived from the soil, or by the decomposition of the sodium potassium tartrate.

and with an alkalinity equal to about 350 parts of nitrogen per million in the case of monosodium carbonate. As far therefore as these few experiments go, the maximum degree of alkalinity which nitrification will tolerate is much the same whether ammonium or monosodium carbonate is the alkaline substance present. On the other hand, when disodium carbonate is the alkaline substance, the limit of alkalinity, though imperfectly ascertained, is distinctly lower. Nitrification has twice certainly occurred with an alkalinity equal to 174 parts of nitrogen per million, and nitrification has more doubtfully occurred in one out of two trials with an alkalinity equal to 261 parts of nitrogen per million.

The prejudicial influence which soluble alkalis exercise on nitrification, when they exceed a certain amount, has been noticed by Schloesing and Müntz (*Compt. rend.*, **89**, 1075). They say "Une faible alcalinité des milieux est nécessaire à la production du nitre. Dans la nature, c'est généralement le carbonate ou plutôt de bicarbonate de chaux qui joue le rôle d'alcali. Les carbonates alcalins très étendus produisent le même résultat; mais, lorsque leur degré de concentration dépasse deux ou trois millièmes, ils deviennent défavorables ou même arrêtent complètement l'action du ferment nitrique. Il en est de même du carbonate d'ammoniaque et de la chaux." No details of their experiments have been published. The proportion of soluble alkalis which I have found to prevent nitrification is smaller than that mentioned by the French chemists, save in the case of monosodium carbonate; of this salt, two-thousandths did not prevent nitrification, but three-thousandths did.

The prejudicial influence of caustic lime on nitrification was noticed long since by Boussingault. The alkalinity of lime-water is indeed about twice as great as that shown in my own experiments as the maximum beyond which nitrification will not occur. A heavy dose of lime applied to land will thus probably retard, or even suspend for a time, the process of nitrification in the surface soil, but this action will soon cease as the lime unites with carbonic acid, and the final result will be favourable to nitrification if the land was originally deficient in lime.

The fact that nitrification will not occur in a solution exceeding a certain degree of alkalinity entirely prevents the nitrification of urine, except when largely diluted with water. The first action of soil organisms upon urine is the conversion of urea into ammonium carbonate; the second action—the nitrification of this ammonia—can only take place if the alkalinity of the solution, and consequently the proportion of ammonium carbonate, is below a certain very moderate amount. The limit imposed by concentration on the nitrification of urine will be seen by the results given in the following table. Pre-

vious experiments had shown that a 10 per cent. solution of urine was nitrifiable, though with some difficulty; further experiments were therefore made to ascertain the extreme limit of concentration at which nitrification would occur. In each experiment, 100 c.c. of diluted urine were placed in a loosely stoppered bottle, and 1 gram of arable soil added. The experiments commenced on May 6, 1884.

Nitric or Nitrous Acid produced in Diluted Urine of various strengths, Seeded with Surface soil May 6, 1884.

Urine in 100 of water.	May 17 (11 days).	May 26 (20 days).	June 23 (48 days).	July 7 (62 days).	Aug. 4 (90 days).	Sept. 30 (147 days).	Oct. 25 (172 days).
1.	trace	small	abundant	—	—	—	—
5.	none	trace	moderate	abundant	abundant	abundant	—
10.	„	none	none	trace	large	abundant	abundant
12.	„	„	„	none	trace	considerable	large
14.	„	„	„	„	none	none	none
16.	„	„	„	„	„	„	„

It is seen that nitrification commenced in the 1 per cent. solution of urine in 11 days; in the 5 per cent. solution in 20 days; in the 10 per cent. in 62 days; and in the 12 per cent. in 90 days. In the solutions of greater concentration, no nitrification has appeared.

The alkalinity of the 10 per cent. urine solution was determined by experiment at the commencement of nitrification, it was equivalent to 351 parts of nitrogen per million. The alkalinity of the 12 per cent. solution was found to be equal to 368 parts of nitrogen per million when nitrification started. The alkalinity of the 14 and 16 per cent. urine solutions on September 6, was equal respectively to 412 and 479 parts of nitrogen per million; in these solutions, no nitrification has up to the present time (November 20) appeared. The greatest alkalinity of a urine solution in which nitrification is possible, is thus equal to about 368 parts of nitrogen per million, a figure identical with that obtained in the previously described experiments made with ammonium carbonate. The idea with which the experiments were started is thus confirmed. The limit of concentration of a urine solution which shall be capable of nitrification is determined by the degree of alkalinity of the solution after the urea is converted into ammonium carbonate. It is of course possible that urine solutions stronger than those here described may finally undergo nitrification if placed in circumstances where a gradual volatilisation of ammonium carbonate will take place. Stronger urine solutions would also probably nitrify

if poured on a considerable mass of soil; partly because the urine would be further diluted by the moisture of the soil, and partly because a part of the ammonia would be removed from solution by the absorptive power of the soil. Strong solutions of urine could probably also be nitrified if mixed with gypsum, by which the injurious excess of ammonium carbonate would be removed, ammonium sulphate being substituted for it.

Some practical bearings of these results are obvious. Alkaline waste liquids may prove a very undesirable addition to streams in which the oxidation effected by living organisms is the natural means of purification. Farmers, too, will now better understand why liquid manures should always be applied to land in a state of great dilution. Where sheep or cattle are fed on land, there is undoubtedly in dry weather a considerable loss of ammonia, the fermented urine remaining on the surface in a condition too concentrated either for nitrification or the retention of the ammonia by the soil. The effect of liming soil will now also be better understood.

2.—*Concentration of the Solution.*

The influence of increased concentration of a solution in retarding, or altogether preventing the process of nitrification, has been already illustrated so far as those solutions are concerned in which, as in the case of urine, an increase of concentration implies an increase in the proportion of soluble alkali present; we have yet to say a few words as to the behaviour of solutions in which difference of concentration is not accompanied by a difference in alkalinity. Such conditions occur when solutions of ammonium chloride of various degrees of concentration are the subject of experiment, calcium carbonate being the only base supplied. In such solutions, it is found that an increase of concentration always retards the commencement of nitrification, this retardation being manifest whenever a strong and weak solution are seeded with equal amounts of organism of similar character, and then placed under identical external conditions. The extent of the retardation depends greatly on the conditions of the experiment. If a small amount of feeble organism is supplied to a weak, and to a more concentrated solution of ammonium chloride—say, for instance, to the solution described on p. 642, and to one of 8 or 16 times the strength—nitrification may commence much earlier in the weaker solution if the temperature is low, but only a few days earlier if the temperature is that most favourable to the growth of the organism. Thus in some experiments described in the previous Report, solutions of the comparative strengths of 1 : 8 were seeded on the same day; at a temperature of 7—10°, nitrification commenced in

the weaker solutions in 31—38 days, and in the stronger in 78 days; whilst at a temperature of 30° nitrification began in the weaker in 11—12 days, and in the stronger in 17—19 days. It has since been ascertained that an increased quantity, or special vigour of the ferment added, also greatly diminishes the hindrance to nitrification presented by a strong solution. It would appear that the nitrifying organism finds difficulty in multiplying in a strong solution; and that this is particularly the case when the organism is of feeble constitution, or has been previously cultivated in a weak solution. An organism of such character may produce no effect when added in small quantity to a strong solution. In one instance of this kind, nitrification had not commenced in 144 days. If, however, the temperature is considerably raised the multiplication of the organism is stimulated, and the results of its work soon appear. By adding a large quantity of the organism, or an organism already cultivated in a strong solution, the difficulty may equally be met without raising the temperature. Thus in an experiment with an ammonium chloride solution of eight times the usual strength, but seeded with 1 gram of fresh soil, nitrification appeared in 16 days at the ordinary temperature. Illustrations of the influence of different kinds and amount of seed will come more fitly in the following section; in every series, however, in which a uniform seeding is adopted nitrification will appear first in the weaker solution.

In the previous Report, the strongest ammonium chloride solution nitrified contained 0·640 gram of the salt per litre. While the system of small seeding was employed, it was found extremely difficult to nitrify stronger solutions. By the use of a more vigorous organism and larger seeding, the limit of concentration has been greatly extended. Solutions containing 1·280 gram of ammonium chloride per litre have been completely nitrified, and nitrification is now in active progress in solutions containing 2 grams, 4 grams, and 8 grams of ammonium chloride per litre. The first of these three solutions contained, besides the ammonium chloride, sodium potassium tartrate, 1 gram; potassium phosphate, 0·3 gram; magnesium sulphate, 0·1 gram per litre. The other two solutions contained twice the quantities just named. To 100 c.c. of each solution was added 1 gram of fresh soil. The experiment commenced on May 19, 1884; no artificial heat was used. Nitrification commenced in the weakest solution in 35 days, in the second solution in 42 days, and in the strongest solution in 56 days. The last-named solution would contain 2095 parts of nitrogen per million. A far stronger solution of ammonium chloride can thus be nitrified than of ammonium carbonate.

3.—*Character and Amount of the Nitrifying Organism.*

The general influence of the character and quantity of the organism has been necessarily mentioned in the preceding section. The subject is of considerable importance: in fact, the rapidity of nitrification very greatly depends on these conditions, and comparative experiments are of little value in which the conditions named have not been maintained as constant as possible. We will first describe some results obtained with different quantities of organism.

Three bottles, each containing 100 c.c. of a $\frac{1}{2}$ per cent. urine solution, were seeded respectively on October 8, 1883, with 1 drop, 5 drops, and 10 drops of a nitrified liquid. On December 13 (66 days after seeding) nitrification had just commenced in the solution which had received 1 drop, it had made considerable progress where 5 drops had been added, and still greater progress where 10 drops had been employed.

Three series of experiments were made in a dilute urine solution (4 c.c. per litre), the seed being limited to one-hundredth of a drop of nitrified solution; this was accomplished by adding 1 c.c. of the nitrified liquid (previously shaken) to 100 c.c. of boiled water, mixing well, and then seeding with 1 drop of the solution. In each series of experiments, a different nitrified liquid was employed as seed. In the first series, only one solution nitrified out of five. In the second series, all the five solutions nitrified, but only after a long time. In the third series, also of five, none of the solutions nitrified.

Three experiments were made with the strong solution containing 2 grams of ammonium chloride per litre, described in the preceding section; 0·01, 0·10, and 1·00 gram of fresh soil were employed as seed. With 1 gram of soil, nitrification started in 35 days, with 0·10 gram in 42 days, and with 0·01 gram in 56 days.

When the seed is of vigorous constitution, a diminution in its quantity is far less severely felt than when seed of feeble character is employed.

The different vigour of the nitrifying organism obtained in different cultivations is a fact that soon strikes an experimenter on nitrification. If two dilute solutions of the same composition have been completely nitrified by the addition of small amounts of organism, it seems fair to conclude that a similar amount of organism will be found in each solution at the close of the experiment, equal amounts of food having been present, and equal amounts of work done; and this probability is increased when second and third cultivations are made from each of these solutions. Notwithstanding, however, this similarity of condition, equal volumes of these two nitrified solutions may possess a

very different capacity for producing nitrification; one may be a strong ferment, starting nitrification in a very short time when added to a new fluid, and the other a weak ferment, extremely slow in action, and these characteristics will remain throughout many successive generations.

The character of the organism is in these cases determined by its previous history. A vigorous organism is obtained by cultivation in a fairly strong solution, well supplied with nutritive ingredients; such an organism will more or less maintain its character even during successive cultivations in a weak solution.

A weak organism is obtained by long repeated re-cultivation in very dilute solutions; by proceeding thus, the organism may at last become scarcely able to produce nitrification at all, even at the most favourable temperature. When a weak organism is placed in a strong nutritive solution, it may produce no effect; but if nitrification sets in it may become vigorous, the new growth of organism gathering strength from the favourable conditions surrounding it.

With the experience thus gained as to the circumstances which determine the vigour of the nitrifying organism, it has been possible, as already stated, to nitrify solutions which before had proved refractory. Thus four solutions, two of 8, and two of 16 times the usual strength (0·64 gram and 1·280 gram of ammonium chloride per litre), were seeded on May 22, 1883, by the addition of 1 per cent. of a previously nitrified solution. On August 4, nitrification had made some progress in the weaker pair of solutions, but had not commenced in the stronger. On October 13 (144 days after seeding), no nitrification had yet appeared in the two stronger solutions. These were now re-seeded, not from the weak solution previously employed, but from the solution of eight times the usual strength, the nitrification of which was now nearly completed. The use of organism grown in this more concentrated solution was quite successful, the solutions of 16 times the usual strength were both nitrified.

The plan that has proved most effective in producing rapid nitrification, is to make use of the sediment lying at the bottom of the vessel in which the nitrification of a fairly strong solution has been conducted. As calcium carbonate is employed in excess in the operation, the sediment largely consists of this substance; but with this, after standing, the greater part of the nitrifying organism is associated. If at the conclusion of nitrification the clear solution is decanted from the sediment, and the new solution which is to be nitrified poured on in its place, conditions extremely favourable for rapid nitrification are obtained. This method ensures the presence of a large quantity of the nitrifying organism, and if the previous cultivation has been made in a fairly strong solution, the organism is also of high quality.

When a pure nitrifying organism, the result of previous cultivation, is not available, the same conditions favourable to rapid nitrification may be obtained by adding sufficient moist arable soil (taken an inch or two below the surface), to slightly cover the bottom of the vessel employed.

Illustrations have already been given of the successful action of large applications of a vigorous organism in the case of solutions far stronger than those previously nitrified; a few examples of the increase of speed resulting from this mode of work may now be added.

100 c.c. of a 2 per cent. urine solution were seeded on October 8, 1883, with two drops of a previously nitrified solution; nitrification was nearly completed on February 5, 1884, 122 days after seeding. At this date, the solution was decanted from the sediment at the bottom of a $\frac{1}{2}$ per cent. urine solution just nitrified, and after washing the sediment once by decantation, 100 c.c. of a 2 per cent. urine solution were introduced. This solution was completely nitrified by March 31, 54 days after seeding, or in far less time than under the previous conditions.

100 c.c. of a 5 per cent. urine solution, seeded as before with two drops of a previously nitrified solution, showed a rather considerable amount of nitrification at the end of 86 days. A similar solution placed on a sediment showed a very large amount of nitrification in 31 days. A solution of similar strength treated with 1 gram of soil showed a commencement of nitrification in 20 days.

On May 8, 1884, 100 c.c. of the usual dilute ammonium chloride solution (see p. 642) were placed on the sediment left after the nitrification of a solution eight times as strong. In nine days, nitrification had made very distinct progress, and in 16 days the whole of the ammonia had disappeared. This is the speediest nitrification I have yet observed in experiments made in solutions; only once has nitrification been completed in 16 days at the favourable temperature of 30°, and generally 19 days are required at this temperature for solutions of similar strength, receiving only a small quantity of seed. The use of a large amount of vigorous organism thus effected nitrification at ordinary temperatures, at a speed equal to the most favourable result previously obtained at optimum temperatures.

There can be no doubt that the extremely rapid nitrification which certain nitrogenous matters undergo in arable soil is largely due to the immense mass of nitrifying organism with which this matter is brought in contact.

4. *Influence of Depth of Solution.*

In the earliest experiments, the solutions were placed in wide-mouthed pint bottles, the column of liquid at starting being 5 inches

deep. The greater number of experiments have, however, been made in smaller bottles, the column of liquid not exceeding a depth of 2 inches. On three occasions a comparison of the two methods was made, the volume of seed added in each experiment being proportional to the bulk of the solution. Out of nine experiments, nitrification was in seven instances considerably more rapid in the shallower liquids, whilst in two cases there was a slight advantage with the deeper solutions. In all cases there was free access of air through a cotton-wool stopper.

There can be no doubt that for vigorous nitrification a rapid renewal of the dissolved oxygen of the solution is required. For this reason nitrification in a stagnant solution can never proceed so rapidly as in a solution which moistens an aërated porous solid. Partly for this reason, though still more for the reason mentioned at the close of the last section, any suitable solution poured upon a mass of porous soil will be nitrified in a far shorter time than has ever been obtained in experiments made with stagnant liquids of considerable depth.

5. *Influence of Proportion of Organic Carbon.*

In the previous Report, three experiments were described in which the solutions contained different proportions of sodium potassium tartrate, the ammonium chloride remaining constant, the phosphates and remaining ingredients varied however with the tartrate. The trials were made at 20°, afterwards raised to 30°. Nitrification commenced first in the solution containing least tartrate (47 per cent. of the ammonium chloride), but concluded first in that containing most tartrate (187 per cent. of the ammonium salt). A few more experiments have been made on the subject.

In 15 pairs of experiments in which the solution was similar to that described on p. 642, excepting that one series received 40 mgrms., and the other 160 mgrms. of sodium potassium tartrate per litre (50 per cent. and 200 per cent. of the ammonium chloride), the advantage as to speed of nitrification was in 7 instances with the larger proportion of tartrate, in 3 instances with the smaller, and in 5 instances the rate of nitrification was quite similar. There was thus on the whole some advantage from the use of the larger proportion of tartrate; probably tartrate 100 per cent. of the ammonium salt is sufficient for every purpose.

Two series of experiments were also made in which glucose was substituted for the tartrate in the usual ammonium chloride solution; the glucose was used in the proportion of 20, 50, 100, and 200 mgrms. per litre. In each series, the solution containing least glucose was the first in which nitrification was completed.

In two pairs of experiments, diluted urine (4 c.c. per litre) was nitrified both with and without the addition of 100 mgrms. of glucose per litre; the rate of nitrification was not distinctly affected by the glucose.

There is thus no advantage to be derived from the presence of organic carbon above the very small proportion essential for the nourishment of the nitrifying organism; indeed the presence of an excess of the carbon compound must tend to diminish the rate of nitrification by appropriating a portion of the otherwise available oxygen. Urine apparently contains quite enough organic carbon for its own nitrification.

Minimum Temperature at which Nitrification occurs.

During the cold winter of 1879–80, some quantitative determinations of nitrous and nitric acids were made in a series of solutions standing in a cold cupboard. The solution was the ordinary one, containing ammonium chloride equal to nearly 21 parts of nitrogen per million. Weekly determinations in four solutions undergoing a nitrous, and in one solution undergoing a nitric fermentation, gave the following results:—

Production of Nitrous and Nitric Acid in Ammoniacal Solutions during a Period of Low Temperature, Nov. 20—Dec. 18, 1879.

	Nov. 20.	Nov. 27.	Dec. 4.	Dec. 11.	Dec. 18.
Mean temperature of preceding week	7°·8	6°·2	4°·0	3°·2	5°·6
Maximum temperature of preceding week	10°·9	7°·2	6°·5	5°·1	6°·4
	Nitrogen as nitrous acid per million.				
Solution N	4·2	6·2	8·8	12·1	16·3
„ N3	5·4	7·9	10·4	13·5	17·2
„ N4	2·2	4·0	5·9	7·8	11·3
„ N5	1·7	2·7	4·6	5·4	7·6
	Nitrogen as nitric acid per million.				
Solution N′4	5·3	5·4	5·8	—	6·8

From these results, it appears that nitrification may proceed slowly

in a solution even at a low temperature; the mean temperature of the coldest week is indeed as low as 3·2°, the maximum temperature during the same period being about 5·1°. It appears that the nitric fermentation was more affected by cold than the nitrous; of this fact, however, we have only a single instance.

The Reduction of Nitrates by Soil.

Of the general conditions under which reduction of nitrates occurs it is not my intention to speak; I wish simply to call attention to the curious fact that when fresh soil is added to diluted urine, or to other solutions suitable for nitrification, a destruction of the nitrates already present precedes the commencement of nitrification. This disappearance of the nitrates is completed in a few days. Dehérain and Maquenne have shown that the reduction of nitrates by soil is accomplished by bacteria. It would appear that the reducing bacterium multiplies itself far more rapidly than the nitrifying bacterium, and runs its course before the other becomes active. The reduction of nitrates now in question is always accompanied by turbidity of the fluid.

The Nitric Acid contained in Human Urine.

In the course of the experiments described in the present paper, I became aware that nitrates are a usual constituent of fresh human urine, the fact has however long been known. If half a cubic centimetre of fresh urine is diluted with its own volume of water, a drop of solution of diphenylamine sulphate added, and then 1 or 2 c.c. of concentrated sulphuric acid, the violet colour characteristic of the presence of nitric and nitrous acid will be produced. It is advisable to stand the beaker, or test-tube, containing the urine, in cold water during the addition of the sulphuric acid, to prevent the charring of the organic matter. As I have failed to find nitrous acid even with the extremely delicate naphthylamine test, it would appear that nitric and not nitrous acid is present. Quantitative determinations, made by Schloesing's method, have given me the following amounts of nitric nitrogen in fresh human urine.

Time of collection.	Nitric nitrogen per million.
October 1883, 11 A.M.	8·18
January 15, 1884, 11 A.M	20·56
June 3, 1884, 8 A.M.	16·23
„ 25, 1884, 8 A.M.	7·08
October 21, 1884, 8 A.M.	4·76

In employing Schloesing's method, it is advisable not to take more

than 25 c.c. of urine, as the amount of carbonic acid produced by the splitting up of the urea is very large.

The amount of nitric acid occurring in urine appears from these determinations to be very variable, and in some cases rather considerable. The origin of this nitric acid is a subject of considerable interest. Bence Jones (*Phil. Trans.*, 1851, ii, 399) maintained that ammonia is oxidised to nitric acid in the human body, and the same conclusion has been recently arrived at by Th. Weyl. That the animal body is an organism possessed of wonderful oxidising powers is well known, and it would perhaps excite little surprise if it were shown that nitrates were produced in the process of oxidation. The evidence brought forward to support this conclusion is however at present very incomplete. That nitrates are present in many articles of food—notably in drinking water, and in most succulent vegetables—is an undoubted fact, and these nitrates, unless destroyed in the system, must appear in the urine; the evaporation from the body will also frequently determine the appearance of nitrates in the urine in a more concentrated form than in the food. To prove that nitrates are normally produced in the human body it would be necessary absolutely to exclude nitrates from the food. This has been partially done by Wulffius, who found that under these circumstances the nitrates in the urine were greatly diminished. The influence of diet probably explains the low contents of nitrate in the last two analyses just quoted; the urine in these cases was collected after a supper of bread and milk only. An entirely different mode of attacking the question is by administering ammonium salts, and observing whether the quantity of nitrates in the urine is increased under these conditions. This mode of inquiry has been adopted both by Bence Jones and by Th. Weyl. Both experimenters distil the urine with concentrated sulphuric acid, and examine the distillate for nitrous acid. Bence Jones seldom found nitrates by this method in normal urine; but after the administration of ammonia, ammonium carbonate, tartrate, or chloride, nitrous acid was found in the distillate by means of potassium iodide and starch; the same result followed the administration of urea. No quantitative experiments were made. Wulffius, on the other hand, found no increase of nitrates to follow the administration of ammonium chloride.

A recent research on the subject has been made by Th. Weyl. A summary of his communication to the Physiological Society of Berlin appears in *Nature* of April 3, 1884, p. 543. Apparently only a portion of the communication has been published, the paper by Th. Weyl, "Ueber die Nitrate des Thier und Pflanzenkörpers" (*Archiv für Pathologische Anatomie und Physiologie und für Klinische Medicin*, 1884, 462), dealing only with the historical part of the subject, and

with his results showing that nitrates are generally present in human urine, but not in that of dogs fed on flesh. According to the summary in *Nature*, Weyl found that in the case of men a very considerable increase in the nitrates of the urine followed the administration of ammonium citrate.

As it appeared of considerable interest to obtain further evidence as to this alleged oxidation of ammonia in the human body, I have made a few experiments with myself as subject. The method employed was to make a comparative experiment on two days of similar diet. At the end of the first day the urine passed between 10 P.M. and 8 A.M. was measured, and the nitric acid present determined. On the second day of similar diet, a known quantity of ammonium salt was taken in distilled water at 10 P.M., and the urine collected as before at 8 A.M., measured and analysed. In each determination, 25 c.c. of urine were evaporated to about 1 c.c., mixed with freshly boiled ferrous chloride and hydrochloric acid, and then distilled to dryness in Schloesing's tube retort, from which all air had previously been expelled. The nitric oxide in the mixed gases obtained was determined with considerable accuracy by the use of a Regnault-Frankland gas analysis apparatus. The results obtained in three comparative experiments, in which ammonium chloride, carbonate, and citrate were administered, were as follows:—

Date (1884).	Ammonium salt taken.	Urine collected 10 P.M. to 8 A.M.	Nitric nitrogen	
			Per million of urine.	Eliminated in urine during 10 hours.
		c.c.		mgrms.
June 3..	None	587	16·23	9·5
„ 4..	Ammonium chloride, 1 gram	785	12·20	9·3
June 25..	None	595	7·08	4·2
„ 26..	Ammonium carbonate, 1 gram	670	5·98	4·0
Oct. 21..	None	650	4·76	3·1
„ 22..	Ammonium carbonate, 2 grams, neutralised with citric acid	910	4·28	3·9

The amounts of nitric nitrogen found per million of urine in each experiment are of little importance, as the degree of concentration of the urine varied a good deal; we must look rather at the absolute quantity of nitric nitrogen eliminated in equal times during each experiment. Thus viewed we find that the production of nitric acid

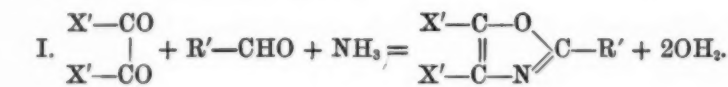
was practically unaffected by the administration of ammonium salts. In the case of ammonium chloride and carbonate, the nitric acid is very slightly diminished by their use, in the case of ammonium citrate it is slightly increased. The experiments with ammonium carbonate and citrate were made on a similar diet.

The few experiments here described appear to lend no support to the theory that ammonia is oxidised to nitric acid in the human body.

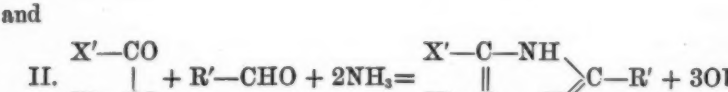
LIII.—*On the Action of Aldehydes and Ammonia on Benzil* (continued).

By Francis R. Japp, M.A., Ph.D., and Samuel C. Hooker.

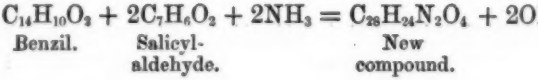
In former communications (this Journal, Trans., 1880, p. 666; 1881, p. 225; 1882, pp. 146, 157, and 323; 1883, pp. 9 and 197), relating to the joint action of aldehydes and ammonia on compounds containing the dicarbonyl-group (—CO—CO—), two general reactions of this class have been described:—



and



In addition to the above, it was mentioned (Trans., 1883, p. 17) that with certain aldehydes a third and totally distinct reaction occurs. Thus benzil, salicylaldehyde, and ammonia react according to the equation—



Benzil.	Salicyl-aldehyde.	New compound.

A precisely similar reaction occurs when furfuraldehyde is substituted for salicylaldehyde.

The present communication is devoted to an account of this new reaction, and to a study of the compound obtained with salicylaldehyde. We venture to think that we have succeeded in throwing light on the constitution of this compound. The general reaction,

corresponding with that in which the compound is formed, may be expressed by the following equation:—

$$\text{III.}\quad \begin{matrix} X'—CO \\ | \\ X'—CO \end{matrix} + 2R'—CHO + 2NH_3 = \begin{matrix} R'—CH—NH—CO—X' \\ | \\ R'—CH—NH—CO—X' \end{matrix} + 2OH_2.$$

This reaction differs from the two foregoing in the fact that, whereas in these the two carbon-atoms of the dicarbonyl-group become doubly linked, in the present reaction, as we shall endeavour to show, the atoms undergo separation, so that the diketone is broken up into two halves, which become two substituting acid radicals in the molecule of the new compound; at the same time the two aldehyde residues become linked by means of the carbon-atoms of the CHO-groups.

In the first two reactions, the aldehyde is oxidised at the expense of the diketone; in the third, the reverse is the case, and the diketone is oxidised at the expense of the aldehyde. Thus, in the hydrolytic decomposition of the compounds formed in equations I and II, the aldehyde part of the molecule is eliminated as the corresponding acid; in the decomposition of the compounds formed in equation III, the diketone residues are liberated as two molecules of an acid having the same radical as the diketone.

The salicylaldehyde compound was selected for study, partly because of the ease with which it could be prepared, but chiefly on account of the readiness with which the various compounds obtained in its decomposition could be identified. According as a salicylic or a benzoic derivative was obtained in any given decomposition of the compound, there was the certainty that the parentage of that portion of the molecule must be ascribed to the aldehyde on the one hand, or to the diketone on the other.

Action of Salicylaldehyde and Ammonia on Benzil.

Equal weights of salicylaldehyde and benzil were dissolved in alcohol with the aid of heat, and the warm solution was saturated with gaseous ammonia. During the process, the new compound separated as a lemon-yellow crystalline powder. In order to prevent the delivery-tube from being choked by the solid substance, the ammonia was passed into the liquid through a wide T-piece, one end of the cross-limb of which was closed by a perforated cork, whilst the other was immersed in the liquid. A glass rod, working air-tight through the cork, served to clear the tube without interrupting the operation.

The saturated liquid was allowed to stand for some hours, after which the substance was filtered off and extracted two or three times with boiling alcohol, in which it is practically insoluble. In this condition it was employed for the various reactions about to be described, although it still retained its yellow colour. The yield in various operations was very constant, and amounted to about three-fourths of the united weights of the benzil and salicylaldehyde employed.

For analysis, a portion was further purified by dissolving it in boiling phenol and precipitating with alcohol, repeating these operations. It was thus obtained as a white crystalline sandy powder, consisting of microscopic plates. When heated in a capillary tube, it becomes dark-coloured at about 260°, and melts with decomposition above 300°. It is almost insoluble in alcohol, ether, glacial acetic acid, and the other ordinary organic solvents. Boiling phenol dissolves it most readily.

Analysis gave figures agreeing with the formula $C_{28}H_{24}N_2O_4$:—

	Substance.	CO_2.	OH_2.
I.	0·1190	0·3237	0·0582
II.	0·1678	0·4550	0·0844

III. 0·1140 gram burnt with copper oxide in a vacuum gave 6·1 c.c. moist nitrogen at 14° and under 761 mm. pressure.

	Calculated for $C_{28}H_{24}N_2O_4$.		Found.		
			I.	II.	III.
C_{28}.....	336	74·34	74·19	73·95	—
H_{24}	24	5·31	5·43	5·59	—
N_2	28	6·19	—	—	6 30
O_4	64	14·16	—	—	—
	452	100·00			

The equation according to which this compound is formed has already been given.

It is remarkable that in the case of parahydroxybenzaldehyde the reaction with benzil and ammonia takes place according to equation II, yielding parahydroxylophine (Trans., 1882, p. 326), whereas, when the isomeric salicylaldehyde is substituted for the para-compound, the reaction takes place as above according to equation III.

Action of Caustic Soda on the Condensation Product.—The compound dissolves in caustic soda. The solution was boiled for several days, at the end of which time nearly the whole of the substance was precipitated unchanged on the addition of hydrochloric acid. Some slight decomposition had, however, taken place, as a small quantity of benzoic acid could be extracted from the acidified liquid by treatment with ether, but no salicylic acid could be detected.

By fusion with caustic soda, the substance yields benzoic and salicylic acids. The former was identified by its fusing point, the latter by the violet coloration with ferric chloride.

Action of Hydrochloric Acid on the Condensation Product.—By heating the compound with dilute hydrochloric acid (fuming acid diluted with twice its volume of water) at a temperature of 210° in sealed tubes for five hours, the benzil portion of the molecule is removed as benzoic acid and the hydrochloride of a new base is obtained. When a more concentrated acid or a higher temperature is employed, the benzoic acid is obtained as before, but the base is resinised, whilst, at a somewhat lower temperature, no action takes place. A large excess of the aqueous acid must be used, as any substance which is not in solution during the reaction is resinised; but even under the most favourable conditions it was found impossible to prevent entirely the formation of resin.

On warming the liquid thus obtained, the benzoic acid and the hydrochloride went into solution, whilst the resin, together with any unaltered substance, remained undissolved. The base precipitated from the filtered solution by the addition of ammonia was contaminated with resin. It was dissolved in an excess of hot benzene, and on cooling the liquid deposited the greater part of the resin. The filtered solution, which was only slightly coloured, was evaporated to a small bulk and, on cooling, yielded the base in a crystalline form. The substance was recrystallised from benzene until the constant fusing point 180·5° was obtained. It is readily soluble in hot benzene, almost insoluble in the cold. It is deposited from the benzene solution in groups of small lustrous laminæ, which are soluble in alcohol, ether, and chloroform. Water dissolves it very slightly, but it is soluble in caustic alkalis.

Analysis gave numbers pointing to the formula $C_{14}H_{16}N_2O_2$:—

	Substance.	CO_2.	OH_2.
I	0·1282	0·3229	0·0764
II	0·1226	0·3084	0·0735

III. 0·0991 gram burnt with copper oxide in a vacuum gave 10·05 c.c. moist nitrogen at 20·3° and under 762·8 mm. pressure.

	Calculated for $C_{14}H_{16}N_2O_2$.		Found.		
			I.	II.	III.
C_{14}.....	168	68·85	68·69	68·60	—
H_{16}	16	6·56	6·62	6·66	—
N_2.....	28	11·48	—	—	11·62
O_2.....	32	13·11	—	—	—
	244	100·00			

This base is formed from the original compound according to the equation:—

$$C_{28}H_{24}N_2O_4 + 2OH_2 = \underset{\text{Base.}}{C_{14}H_{16}N_2O_2} + \underset{\text{Benzoic acid.}}{2C_7H_6O_2}.$$

We shall show later that the original condensation product is a dibenzoyl-derivative of this base.

The preparation of any considerable quantity of the base by the foregoing method is a matter of great difficulty, but farther on a method will be described by which the base can be obtained with relative ease. The salts were prepared from a specimen of base obtained by this second method.

The *platinichloride** is deposited in large transparent orange-coloured crystals, consisting of thick rhomboïdal plates with bevilled edges, when platinic chloride is added in excess to a solution of the hydrochloride, and the liquid is evaporated over sulphuric acid. The presence of an excess of hydrochloric acid is to be avoided, as it causes the salt to be contaminated with hydrochloride, which is less soluble in the concentrated acid than the platinichloride. The crystals contain water of crystallisation. They are permanent in air, but effloresce over sulphuric acid and become anhydrous at 100°.

0·5026 gram crystallised salt lost on heating to 100° 0·0501 gram.

	Calculated for $C_{14}H_{16}N_2O_2,2HCl,PtCl_4,4OH_2$.	Found.
Water in 100 parts	9·89	9·97

0·2134 gram anhydrous salt left on ignition 0·0638 gram platinum.

Calculated for $C_{14}H_{16}N_2O_2,2HCl,PtCl_4$.	Found.
30·03	29·90

The *hydrochloride* is obtained as a crystalline powder, consisting of microscopic plates, when concentrated hydrochloric acid is added to a saturated solution of the base in dilute hydrochloric acid. It has a pungent, bitter taste, perceptible even with very dilute solutions.

The normal *sulphate* crystallises in prisms, very soluble both in water and in alcohol.

The *picrate* is precipitated in microscopic needles when an aqueous solution of picric acid is added to the solution of a salt of the base. It is practically insoluble in cold water, and dissolves only very slightly on boiling.

* The term "platinichloride," as being more systematic, is here applied to the compounds containing *platinic* chloride, $PtCl_4$.

When fused with caustic soda, the base yields salicylic acid as sole organic product.

As regards the constitution of this base, it is evident from its mode of formation (see equation) that it contains the whole of the salicylic portion of the molecule of the original compound. It therefore contains the group $(C.C_6H_4.OH)'''$ twice, and may be formulated $(C.C_6H_4.OH)_2N_2H_6$. It is very improbable that in the processes in which this compound has been formed a union of the nitrogen-atoms with each other can have occurred; and the only alternative is to assume a union of the salicylic complexes, in which case the compound would have the formula—

$$\begin{array}{l} C_6H_4(OH).CH.NH_2 \\ \quad\quad\quad\quad\quad | \\ C_6H_4(OH).CH.NH_2. \end{array}$$

A compound of this constitution might be designated *dihydroxystilbenediamine*, a name constructed on the analogy of *ethylenediamine*.

The above formula accounts for the diacid character of the base, for its solubility in caustic alkalis, for the fact that it yields salicylic acid by fusion with caustic soda, and for the formation of the various compounds described farther on.

We sought for confirmation of this constitution in the action of nitrous acid on the compound. On adding a dilute solution of sodic nitrite to an acidulated solution of the base, gas was evolved and a neutral body separated, which, by crystallisation from benzene, was obtained in colourless microscopic octahedra. The quantity was unfortunately too small for further examination, the greater part of the base being resinised in the process. The failure was possibly due to the presence of the hydroxyl-groups; by the action of hydriodic acid, however, it may be possible to convert the base into the non-hydroxylated compound, stilbenediamine, and this, with nitrous acid, may perhaps yield hydrobenzoïn, thus definitively proving the constitution of the compound. These reactions will be studied by one of us as soon as the base has been obtained in sufficient quantity.

A systematic study of the reactions of the base, as compared with those of the orthodiamines of the benzene series, will also be undertaken. The base, as containing two amido-groups attached to contiguous carbon-atoms of a fatty chain, is a fatty analogue of an orthodiamine. It will be of special interest to ascertain whether the characteristic condensations in the ortho-series, of diamines with acids, aldehydes, &c., occur in the case of this compound. The analogy between benzene compounds of the ortho-series and certain fatty compounds, an analogy exemplified in the case of the phthalic and succinic compounds, of phthalide and the γ-lactones, of the

anhydro-bases and glyoxaline, and in many other cases, points to a possibility of the occurrence of such reactions.

Action of Acetic Anhydride on the Condensation Product.—A quantity of the condensation product was boiled with twice its weight of acetic anhydride until the whole had dissolved, a process which required about six hours for completion. As soon as this happens, the boiling must be interrupted, since by the continued action of the anhydride the derivative first produced undergoes a further transformation, yielding a compound to be described farther on. On cooling, the new substance separated from the dark solution in colourless rhomboïdal laminæ. These were washed with alcohol and recrystallised from boiling acetic acid, from which they were deposited in the foregoing forms. The substance melted at 225—227°. The melting point was not altered by further recrystallisation. This compound is only sparingly soluble in boiling alcohol, separating in thin rhomboïdal lustrous laminæ.

Analysis gave figures pointing to a diacetyl-derivative,

$$C_{28}H_{22}(C_2H_3O)_2N_2O_4:—$$

	Substance.	CO_2.	OH_2.
I	0·1120	0·2929	0·0527
II	0·1258	0·3288	0·0601

III. 0·1776 gram burnt with copper oxide in a vacuum gave 8·35 c.c. moist nitrogen at 23·5° and under 759·5 mm. pressure.

	Calculated for $C_{28}H_{22}(C_2H_3O)_2N_2O_4$.		Found.		
			I.	II.	III.
C_{32}	384	71·64	71·32	71·28	—
H_{26}	28	5·22	5·23	5·31	—
N_2	28	5·22	—	—	5·28
O_6	96	17·92	—	—	—
	536	100·00			

Hot dilute caustic potash dissolved the compound, at the same time removing the acetyl-groups: hydrochloric acid added to this solution precipitated the original condensation product.

The acetic anhydride mother-liquor from the diacetyl-derivative contained benzoic acid (or benzoic anhydride) derived from the decomposition of a portion of the substance, and also a mixture of compounds sparingly soluble in alcohol. We could not succeed in separating these last from one another. By long boiling with acetic anhydride they are converted into the compound described in the following paragraph.

By continuing the boiling of the condensation product with acetic anhydride for about eight hours after the whole of the substance had passed into solution, a totally different compound was obtained. On cooling, the dark-coloured liquid deposited a crystalline substance, which was washed with acetic acid and then recrystallised from this solvent until the melting point remained constant. It was thus obtained in thin colourless prismatic crystals containing acetic acid. After expelling the acetic acid by heating at 130° the compound melted at 216—219°. The yield was about two-fifths of the weight of the condensation product taken. Analysis of the substance dried at 130° gave figures agreeing with the formula $C_{22}H_{24}N_2O_6$:—

	Substance.	CO_2.	OH_2.
I	0·1391	0·3254	0·0757
II	0·1223	0·2855	0·0647

III. 0·1338 gram burnt with copper oxide in a vacuum gave 8·76 c.c. moist nitrogen at 28·7° and under 755 mm. pressure.

	Calculated for $C_{22}H_{24}N_2O_6$.		Found.		
			I.	II.	III.
C_{22}.....	264	64·08	63·80	63·67	—
H_{24}	24	5·82	6·05	5·88	—
N_2.....	28	6·80	—	—	7·10
O_6.....	96	23·30	—	—	—
	412	100·00			

The compound dissolves readily in hot alcohol and, on cooling, is deposited in thin colourless prisms containing 1 mol. of alcohol of crystallisation.

1·5322 grams of the substance, crystallised from alcohol and air-dried, lost on heating at 120° 0·1496 gram.

	Calculated for $C_{22}H_{24}N_2O_6,C_2H_6O$.	Found.
Alcohol in 100 parts	10·04	9·76

We further satisfied ourselves that the compound $C_{22}H_{24}N_2O_6$ is formed from the pure diacetyl compound by long boiling with acetic anhydride. It may also be readily obtained by heating the original condensation product with acetic anhydride in a sealed tube at 150° for about four hours. At this higher temperature, the transformation is very complete.

The acetic anhydride mother-liquor, which remained after the separation of the compound $C_{22}H_{24}N_2O_6$, contains large quantities of benzoic acid (or benzoic anhydride). After expelling the excess of

acetic anhydride, the residue dissolved almost completely in boiling sodic carbonate, and, on adding hydrochloric acid, the benzoic acid was precipitated. It was identified by its fusing point and other characteristic properties.

The formation of the compound $C_{22}H_{24}N_2O_6$ from the original condensation product may be accounted for as follows. In the first place the diacetyl-derivative is formed; this is then further acted on by acetic anhydride according to the equation—

$$\underset{\text{Diacetyl-derivative.}}{C_{28}H_{22}(C_2H_3O)_2N_2O_4} + \underset{\text{Acetic anhydride.}}{\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}>O} = \underset{\text{Second acetyl-derivative.}}{C_{22}H_{24}N_2O_6} + \underset{\text{Benzoic anhydride.}}{\begin{matrix}C_6H_5.CO\\C_6H_5.CO\end{matrix}>O.}$$

The simplest interpretation of this reaction would be that two benzoyl-groups in the diacetyl-derivative have been replaced by two acetyl-groups. If we therefore formulate the compound $C_{22}H_{24}N_2O_6$ as a tetracetyl-compound, thus:—

$$C_{14}H_{12}(C_2H_3O)_4N_2O_2,$$

it appears as a tetracetyl-derivative of a compound $C_{14}H_{16}N_2O_2$. This is however the formula of *dihydroxystilbenediamine*. The reactions of the compound $C_{22}H_{24}N_2O_6$, which we are about to describe, show it to be *diacetyl-diacetoxystilbenediamine*:—

$$\begin{matrix}C_6H_4(O.C_2H_3O).CH.NH(C_2H_3O)\\ \quad\quad\quad\

	Substance.	CO_2.	OH_2.
I	0·1262	0·3042	0·0714
II	0·1353	0·3263	0·0755

III. 0·1462 gram burnt with copper oxide in a vacuum gave 10·3 c.c. moist nitrogen at 19° and under 768·8 mm. pressure.

	Calculated for $C_{18}H_{20}N_2O_4$.		Found.		
			I.	II.	III.
C_{18}.....	216	65·85	65·74	65·78	—
H_{20}	20	6·10	6·29	6·20	—
N_2.....	28	8·54	—	—	8·19
O_4.....	64	19·51	—	—	—
	328	100·00			

The action of the potash had therefore been to remove two acetyl-groups. These must be the two acetyl-groups attached to oxygen, as their removal constitutes the condition of the solubility of the compound in alkalis. The new compound would thus be *diacetyldihydroxystilbenediamine*, and would have the constitution—

$$C_6H_4(OH).CH.NH(C_2H_3O)$$
$$|$$
$$C_6H_4(OH).CH.NH(C_2H_3O)$$

We shall show later on that the original condensation-product, which in its physical properties (high fusing point, sparing solubility, &c.) closely resembles the present compound, is the corresponding dibenzoyl-derivative of the base—*dibenzoyldihydroxystilbenediamine.*

By boiling the compound $C_{22}H_{24}N_2O_6$ with strong potash for about an hour, all four acetyl-groups were removed, and the base dihydroxystilbenediamine was formed. This was separated by acidifying the solution with hydrochloric acid, and then precipitating with ammonia. A considerable quantity of resin was formed by the action of the strong potash, which rendered the purification of the base a matter of difficulty. For this reason, the melting point was found too low, namely, 175° instead of 180·5°. A microscopic examination of the crystals showed that they had exactly the same forms as those of the base already described. All doubt as to the identity of the two products is dispelled by the result of the action of hydrochloric acid on the compound $C_{22}H_{24}N_2O_6$, a reaction by which the base can readily be obtained in a state of purity.

Action of Hydrochloric Acid on the Compound $C_{22}H_{24}N_2O_6$.—Fuming hydrochloric acid dissolved the compound in the cold. On standing, and more rapidly on heating, the solution deposited a white crystalline

substance. The physical properties of this pointed to its identity with diacetyldihydroxystilbenediamine, the compound obtained by the foregoing action of dilute potash. The substance, after being dissolved in phenol and precipitated with alcohol, yielded on analysis figures agreeing with the required formula $C_{18}H_{20}N_2O_4$. (Percentages: calculated, C = 65·85, H = 6·09; found, C = 65·66, H = 6·23.)

By heating the compound $C_{22}H_{24}N_2O_6$ for three hours with concentrated hydrochloric acid in sealed tubes at 120°, the four acetyl-groups were removed and dihydroxystilbenediamine was obtained. On cooling, the tube contained large crystals of the hydrochloride. This method of preparing the base gives much better results than the direct decomposition of the original condensation compound with hydrochloric acid. In practice the compound $C_{22}H_{24}N_2O_6$ yields about half its weight of pure base. The base, liberated from the hydrochloride by ammonia, was purified as before by crystallisation from benzene.

The material employed in the various experiments, and in the preparation of the salts of the base, was prepared by the foregoing method.

Action of Benzoic Anhydride on the Condensation Product.—A quantity of the compound was heated with excess of benzoic anhydride until the whole had liquefied. The cooled product of the reaction was treated with alcohol, to remove benzoic anhydride and benzoic acid. The undissolved portion was recrystallised from acetic acid, and was thus obtained in colourless microscopic plates, which melted at 246—248°.

Analysis gave figures agreeing with the formula of a dibenzoyl-derivative, $C_{28}H_{22}(C_7H_5O)_2N_2O_4$:—

	Substance.	CO_2.	OH_2.
I	0·1656	0·4607	0·0734
II	0·1490	0·4151	0·0664

III. 0·1882 gram burnt with copper oxide in a vacuum gave 7·1 c.c. moist nitrogen at 22·7° and 765·5 mm. pressure.

	Calculated for $C_{28}H_{22}(C_7H_5O)_2N_2O_4$.		Found.		
			I.	II.	III.
C_{42}.....	504	76·36	75·87	75·98	—
H_{32}	32	4·85	4·92	4·95	—
N_2.....	28	4·24	—	—	4·29
O_6.....	96	14·55	—	—	—
	660	100·00			

As it was important, from the point of view of the proof of the constitution of the condensation product which we are about to give,

to show that no rearrangement of the atoms of the original molecule had taken place during the formation of this dibenzoyl-derivative, beyond the introduction of the benzoyl-groups, we converted this derivative back into the condensation product. This was accomplished by boiling the compound with dilute caustic potash (1 part of caustic potash dissolved in 8 parts of water) until nearly the whole had passed into solution, a process which required several hours. From the filtered liquid, hydrochloric acid precipitated a white substance, which, after crystallisation from phenol, had all the physical properties of the original condensation product, and on analysis yielded figures agreeing with the required formula, $C_{28}H_{24}N_2O_4$. (Percentages: calculated, C = 74·33, H = 5·31; found, C = 74·54, H = 5·49.)

Action of Acetic and Benzoic Anhydrides on Dihydroxystilbenediamine.—In the foregoing pages we have regarded the original condensation product, and a number of the compounds obtained from it, as derived from the base dihydroxystilbenediamine by the replacement of hydrogen by acid radicles. The facts adduced in support of this view have been chiefly analytical.

The experiments about to be described furnish confirmatory evidence by the synthetic production of these compounds from the base.

A portion of the base was treated with acetic anhydride in the cold. A reaction immediately took place, with development of heat, and a very sparingly soluble white compound was formed, which by its physical properties was recognised as diacetyldihydroxystilbenediamine.

A fresh quantity of the base was heated in a sealed tube with acetic anhydride for several hours at 150°. In this way, diacetyldiacetoxystilbenediamine was obtained. It was deposited from its hot alcoholic solution in the characteristic thin colourless prisms, which, after heating to expel the alcohol of crystallisation, melted at 216—219°.

A quantity of the base was heated with benzoic anhydride. At first the whole fused; then, almost immediately, a difficultly fusible substance separated. This was in all probability the original condensation-product, which had thus been regenerated; but, as the quantity of base at our disposal was limited, we preferred to carry the reaction further and obtain the dibenzoyl-derivative of the condensation-product, which can be more readily purified than the condensation-product itself. The heating was therefore continued until the whole had again fused, after which the operation was interrupted. The product of the reaction was treated with alcohol, and the insoluble portion was crystallised from acetic acid. The compound was thus obtained in microscopic plates indistinguishable from those of the dibenzoyl-derivative of the condensation-product and, like these, melting at 246—248°.

The dibenzoyl-derivative of the condensation-product,

$$C_{28}H_{22}(C_7H_5O)_2N_2O_4,$$

is therefore identical with the tetrabenzoyl-derivative of the base. It would thus have the formula—

$$\begin{array}{l} C_6H_4(O.C_7H_5O).CH.NH(C_7H_5O) \\ \quad\quad\quad\

	Substance.	CO_2.	OH_2.
I	0·1518	0·3989	0·0694
II	0·1256	0·3301	0·0586

III. 0·1943 gram burnt with copper oxide in a vacuum gave 12·2 c.c. moist nitrogen at 18·5° and under 757 mm. pressure.

	Calculated for $C_{24}H_{20}N_2O_4$.		Found.		
			I.	II.	III.
C_{24}.....	288	72·00	71·67	71·68	—
H_{20}	20	5·00	5·08	5·19	—
N_2.....	28	7·00	—	—	7·20
O_4.....	64	16·00	—	—	—
	400	100·00			

The following equation, which exactly corresponds with that in which the compound from salicylaldehyde is formed, expresses the reaction:—

$$\underset{\text{Benzil.}}{C_{14}H_{10}O_2} + 2\underset{\text{Furfuraldehyde.}}{C_5H_4O_2} + 2NH_3 = \underset{\text{New compound.}}{C_{24}H_{20}N_2O_4} + 2OH_2.$$

The second compound formed in the above process was purified by recrystallisation from alcohol until the melting point remained constant. It was deposited from its solution in boiling alcohol in tufts of silky needles melting at 246°. Analysis showed that this compound possessed the same percentage composition as the foregoing:—

	Substance.	CO_2.	OH_2.
I.....	0·1163	0·3061	0·0533

II. 0·1328 gram burnt with copper oxide in a vacuum gave 8·8 c.c. moist nitrogen at 21·3° and under 752·5 mm. pressure.

	Calculated for $C_{24}H_{20}N_2O_4$.		Found.	
			I.	II.
C_{24}	288	72·00	71·78	—
H_{20}.....	20	5·00	5·09	—
N_2	28	7·00	—	7·45
O_4	64	16·00	—	—
	400	100·00		

We have as yet made no experiments to ascertain the nature of this isomerism.

The study of these reactions, including those of dihydroxystilbenediamine already indicated, will be continued.

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LIV.—*Modifications of Sodium Sulphate.*

By Spencer Umfreville Pickering, M.A. Oxon., Chemical Lecturer at Bedford College.

Although the heat of dissolution of metallic sulphates has been studied perhaps more fully than that of any other class of salts, much still remains to be done. Many of the existing data rest on the authority of Graham, and, as Person observed in 1851, lack that accuracy which is at present attainable, and which is necessary for the deduction of any general conclusions; whilst in other instances where numbers are given by such eminent observers as even Berthelot, Thomsen, and Favre, we find occasional discrepancies, such as—

$MgSO_4,H_2O + Aq = 13{,}300$ c. (Thomsen), and $= 10{,}986$ c. (Favre);
$Na_2SO_4 + Aq = 170$ c. (Favre), and $= 780$ c. (Berthelot);
$K_2Mg(SO_4)_4 + Aq = 10{,}602$ c. (Thomsen), and $= 7000$ c. (Graham);

which are too large to be attributed to experimental error, and, therefore, require explanation.

In an investigation of the causes of the last-mentioned discrepancy, the author was led to the conclusion that two, and in some cases even three, distinct modifications of double sulphates of the magnesian and alkali metals exist, and, before pursuing the subject farther, it appeared desirable to ascertain whether the single sulphates also may not exist in various forms. The investigation of anhydrous sodium sulphate from this point of view forms the subject-matter of the present communication. Berthelot's paper on "Les sels doubles préparés par fusion" (*Ann. Chim. Phys.*, **29**, 295) had, unfortunately, not come under the author's notice until after his work had been nearly completed.

The calorimetric apparatus employed was an exact production of that described by Berthelot (*Mec. Chim.*, t. i, p. 140). The thermometers were divided into 1 mm. divisions, with a value of 0·04° each, hence one estimation figure would have a value of 0·004.

The quantity of water used for the dissolution of single salts was double that used by Berthelot, namely, 420 H_2O to one molecule, or 600 c.c. to about 10 grams; with double salts, twice this proportion of water was taken. An error of one estimation figure in the reading of the thermometer will give an error of 32 cal. in the molecular heat of solution of a single sulphate, and 64 cal. in that of a double sulphate; the actual variation in results observed

in repeating experiments with the same sample was found to be 28 cal. above or below the mean with the former (deduced from 58 experiments), and ±49 cal. with the latter (from 28 experiments).

The ordinary chemical symbols and atomic weights (as published by Lothar Meyer) are here employed, and the molecular heats given will consequently be expressed by numbers twice as big as those given by Berthelot in similar cases.

The heat of dissolution of anhydrous sodium sulphate ($Na_2SO_4 + 200H_2O$) was given in 1873 by Thomsen as −60 cal. at 18°, subsequently, however, he ascertained that the specimen then used was not quite anhydrous, and in 1878 (*J. pr. Chem.*, **17**, 171) he gave the three following values:—

(1.) 233 cal. at 17—18·5°, prepared by heating $Na_2SO_4.H_2O$.
(2.) 170 „ „ effloresced, and then heated.
(3.) 460 „ „ melted.

The non-concordance of these numbers is attributed to experimental error by Berthelot (*Ann. Chim. Phys.*, **14**, 445), who gives 780 and −190 cal. at 21·5° and 3·2° C. respectively as the values which he obtained with a sample which had effloresced and had then been heated at 200°. With a sample which had been melted he found 1280 cal. at 12·32° when used at once, and 1040 cal. at about 16° with the same sample after it had been kept for two months (*Ann. Chim. Phys.*, **29**, 310).

In order to investigate the matter fully, a large quantity of sodium sulphate was allowed to effloresce until nearly anhydrous, and then powdered very finely: various portions of this were then dried thoroughly at different temperatures. In every case the percentage loss during desiccation was identical, and, further, a portion of each specimen on being heated to redness did not lose in weight; the preparations, therefore, were all perfectly anhydrous.

The following results were obtained; the temperature of the calorimetric water before the introduction of the salt being 20·378° ±0·05.

Specimen.	Molecular heat of dissolution.
1. Dried at about 20° over hydrogen sulphate	47 cal.
2. Dried at 100°	50 „
3. Ditto. The crystalline salt having been melted during the drying.	68 „
4. Dried at 150.....	61 „
Mean	57 „

Specimen.	Molecular heat of dissolution.
5. Dried at 200°	571 cal.
*6. Ditto do.	666 „
7. Dried at a temperature a little below redness	759 „
*8. Dried at a bright red heat	762 „
Mean	760 „
9. Melted two hours before dissolution, and powdered finely.....	863 „
10. Melted two hours before dissolution, and used in one lump	850 „
Mean	857 „

From these results it is evident that there are two modifications of sodium sulphate: all the specimens which had been heated at 150° and lower temperatures give 57 cal. as the value of the equation $Na_2SO_4 + 420H_2O$ at 20·4° C., with an extreme variation of only $\pm$11 cal. When heated, however, to a temperature between 150° and 200° sodium sulphate undergoes a change which, although nearly complete at the latter temperature, is not quite so; this second modification, which dissolves with development of 760 cal., remains unaltered when heated to any temperature below its melting point, and, indeed, even fusion does not appear to change it, the slightly higher numbers obtained with the fused specimens being due, no doubt, according to Berthelot's researches on fused salts (*Ann. Chim. Phys.*, **29**, 312), to the retention of some of the heat of fusion.

The modification which dissolves with the smaller heat-development is, no doubt, from the method of its preparation, the one which corresponds more nearly in constitution with the hydrated salt, and may, therefore, be termed the normal salt or α-Na_2SO_4; this in passing into the other modification absorbs 703 cal., the reaction being endothermic. The second modification, or β-Na_2SO_4, does not appear to change on being kept: a determination of its heat of dissolution two and a half months after its preparation gave 671 cal. above that of the normal salt, sensibly the same as the 703 cal. found at first. The fused salt, however, behaves differently; one of the preparations mentioned in the above table gave only 438 cal. above the normal after a lapse of three months.

* These samples were prepared from a totally different specimen.

The existence of the salt in two different forms will explain the various results obtained by Thomsen; his numbers when reduced to a temperature of 20·4° become 411, 289, and 650 cal. respectively, all of them numbers which would be obtained by taking various mixtures of the two modifications. Berthelot's sample prepared at 200° gives 724 cal. (reduced to 20·4°), a value differing but little from the values given in the above table for similar preparations. Berthelot's fused salt, however, gave numbers (1664 cal. at first, and 1244 cal. after being kept for two months, reduced to 20·4°) larger than any here obtained,* and which might suggest the existence of a third modification: Berthelot's paper itself, however, is a sufficient proof that much weight cannot be attached to the absolute results obtained with fused salts, since they often retain a considerable amount of heat of fusion, and undergo a change not only on being kept, but also on being pulverised, and, as will be shown hereafter, on being cooled more or less quickly. At any rate, it would be unsafe at present to assume the existence of more than two distinct modifications.

Thomsen (*J. pr. Chem.*, **18**, 5) determined the heat of dissolution of sodium sulphate dehydrated to various degrees, and found that nine of the ten molecules of water of crystallisation were combined with an energy represented by 1873 cal. (or 285 cal. with H_2O solid), whilst the remaining molecule combined with a development of 2360 cal.; whence he concludes that a definite monohydrate exists. If, however, we take the heat of dissolution of the normal anhydrous sulphate, −60 cal. at the temperature of his experiments, instead of that of the fused salt, 460 cal., which he takes, we get 1960 cal. as representing the heat of combination of this last molecule, a number sufficiently near the mean value of the others (1873) to show that all the molecules of water have a similar value, and that calorimetric determinations indicate the existence of no hydrate other than the ordinary decahydrate.

Additional Note.—Since the above was written, the anhydrous sodium sulphate precipitated by boiling a saturated solution of the salt has been examined. The precipitated sulphate was dried on a porous tile and exposed to dry air for some days; the adhering decahydrate effloresced under this treatment, and was removed from the crystalline portion by means of a sieve: after exposure to sulphuric acid, this latter gave the following results when dissolved in water at 20·4°:—

Dried over sulphuric acid at 150°	63 cal.
After being heated to redness	777 „

* Indeed in one case a fused specimen gave a number considerably lower than those in the table, namely, 645 cal. at 20·4° (deduced for an experiment at 14°).

numbers which show that it is identical with the normal sulphate, both as regards its heat of dissolution, and also the changes which it undergoes when heated to high temperatures.

LV.—*On some Vanadates of the Amines.*

By G. H. Bailey, B.Sc. (Dalton Chemical Scholar, Owens College).

A comparative examination of the characters of the vanadates of the alkalis* shows that they present marked and interesting differences indicative of the relations which hold between the various members of this group and between these and allied members of other groups. These differences are apparent on comparing the vanadates of potassium, sodium, ammonium, and lithium. The amines containing fatty radicals are also related on the one hand to ammonia and on the other to the alkalis proper, being at the same time strongly basic in their character. It, therefore, seemed desirable in the first place to ascertain whether vanadates of the amines could be prepared, and, if so, whether relationships exist between monamines, diamines, and triamines containing the same or different radicals, which would throw light on the differences observed between the various members of the alkali-group. When it was found, moreover, that the acid vanadates of these amines occur in large and definite crystals, it became a matter of interest to see how far the crystalline form was influenced in the passage from monamine to diamine and triamine, or by the introduction of different basic radicals.

The earlier experiments were made with a solution of "trimethylamine," for which I was indebted to the kindness of M. C. Vincent. M.M. Duvillier and Buisne have found large quantities of dimethyl-

* It may be remarked that if we write the vanadates thus:—xR'_2O, yV_2O_5, the whole of the complicated vanadates can be represented as a series by taking $x = 6$, and y consecutive whole numbers between 2 and 18 (11, 13 and 17 being alone wanting). We have in fact a very complete example of multiple relations. Thus the vanadates of sodium may be written:—

$6Na_2O,2V_2O_5$; $6Na_2O,3V_2O_5$; $6Na_2O,6V_2O_5$; $6Na_2O,9V_2O_5$;
$6Na_2O,12V_2O_5$; $6Na_2O,15V_2O_5$; $6Na_2O,16V_2O_5$; $6Na_2O,18V_2O_5$,

the known numbers of the series.

Na vanadates being those in which					$y = 2, 3, 6, 9, 12, 15, 16, 18.$
K	,,	,,	,,	,,	$y = 3, 5, 6, 9, 12, 18.$
Am	,,	,,	,,	,,	$y = 6, 12, 14, 15, 18.$
Li	,,	,,	,,	,,	$y = 2, 3, 4, 6, 7, 8, 9, 10.$

amine and other homologues in a sample of such trimethylamine from the *vinasse*, it is, therefore, worthy of remark that the sample above referred to proved to be of a similar character, although it will be seen that a second sample was practically pure.

It was essential that pure amines free from other homologues should be used in the work, particulars, therefore, are given of the material used.

Vanadic Acid.—This was part of that prepared by Professor Roscoe in his researches on vanadium, and I am indebted to him for a liberal supply of it.

Trimethylamine.—One of the specimens illustrative of the *vinasse* industry, and labelled "Trimethylamine hydrochloride," consisted principally of fine white crystals sometimes several inches in length, the remainder being a clear liquid. A sample of the liquid and one of the crystals was precipitated as platinochloride; the determinations made were :—

0·444 gram of crystals gave 0·221 gram of CO_2 and 0·156 gram of H_2O.
0·4657 gram of liquid gave 0·235 gram of CO_2 and 0·165 gram of H_2O.
0·3993 gram of crystals gave 0·147 of platinum on ignition.
0·4075 „ liquid „ 0·150 „ „

	Crystals.	Liquid.	Calculated for $2N(CH_3)_3HCl,PtCl_4$.
C	13·57	13·75	13·66
H	3·89	3·93	3·79
Pt	36·81	36·81	36·98

A qualitative examination was further made for secondary amines by the nitrous acid reaction, and for primary amines by the carbamine reaction.

There were no secondary amines, and only the merest trace of primary amines. The substance was, therefore, pure trimethylamine hydrochloride, and from it a solution of the free base was made by distillation with potash.

Dimethylamine.—This was prepared from dimethylaniline of great purity by treating it with nitrous acid, and then distilling the hydrochloride of nitrosodimethylaniline with caustic soda.

The platinochloride gave the following numbers on analysis :—

0·3498 gram gave 0·1417 gram of CO_2 and 0·117 gram of H_2O.
0·5225 „ 0·203 „ platinum on ignition.

	Found.	Calculated for $2N(CH_3)_2H_2Cl,PtCl_4$.
C	9·61	9·62
H	3·29	3·21
Pt.....	38·86	39·05

The remaining amines used were obtained from Messrs. Kahlbaum, and in each case their purity was tested.

Preparation of the Salts.—The general method of procedure was to add the vanadic acid to the solution of the amine in small successive portions in a stoppered bottle, the temperature not being allowed to rise. The first portions of the vanadic acid dissolved to a clear solution, but of those subsequently added a small portion remained undissolved, and was partially reduced to the dark green oxide. In preparing solutions for the ortho-, pyro-, and meta- salts, no oxidising agent was added, and the supernatant liquid remained colourless. In the case of the acid vanadates, the reduction of the vanadic acid was avoided by the addition of an oxidising agent. A solution of hydroxyl being found suitable for the purpose, this was added from time to time, the supernatant liquid becoming of a bright orange-red colour. A little acetic acid facilitated the process, but in the case of the triamines it was unnecessary. The filtered solution was in every case concentrated in a vacuum over sulphuric acid until it crystallised: all evaporations had to be done in this way, as even gentle heating brought about a degradation of the white into the red vanadates, whilst the red vanadates were liable to partial reduction.

Ortho- and Pyro-vanadates.—Several attempts were made to prepare these vanadates but without success; the liquids to which the vanadic acid had been added in the required proportion gave viscous or amorphous masses, which would not crystallise, and on further treatment became converted somewhat rapidly into acid vanadates.

Metavanadates.—On evaporating the colourless liquid obtained by adding vanadic acid to the amine in equal molecular proportions, the metavanadate separates out in crystalline masses which show independent crystal forms. In the case of the monamines they are perfectly white, but are darkened superficially on exposure to sunlight. None of the metavanadates contain water of crystallisation.

(1.) *Methylamine metavanadate.*—$N(CH_3)H_3.VO_3$, on analysis,

0·480 gram gave 0·160 gram of CO_2 and 0·1985 gram of H_2O.

0·5275 ,, 0·365 ,, V_2O_5.

	Found.	Calculated.
C	9·09	9·14
H	4·60	4·57
V_2O_5.....	69·20	69·51

(2.) *Ethylamine metavanadate.*—$N(C_2H_5)H_3,VO_3$, on analysis,

0·369 gram gave 0·223 gram of CO_2 and 0·184 gram of H_2O.
0·3442 „ 0·2155 „ V_2O_5.

	Found.	Calculated.
C	16·48	16·53
H	5·53	5·52
V_2O_5	62·61	62·81

(3.) *Dimethylamine metavanadate*, $N(CH_3)_2H_2.VO_3$, differs from the above, in that some care is needed to prevent its partial transformation into the acid vanadate. However, by exposing the solution to the air as little as possible during the preparation, and conducting the concentration in a rather deep vessel, the salt separates out in a crust on the surface, and in hard rounded tufts of definite crystals on the sides of the vessel beneath the crust. The mother-liquor is drained off, and the crystals, which are only slightly deliquescent, are washed with a little water and finally with absolute ether. They are faintly yellowish and translucent. Analysis :—

0·521 gram gave 0·2885 gram of CO_2 and 0·2435 gram of H_2O.
0·5045 „ 0·3145 „ V_2O_5.

	Found.	Calculated.
C	16·43	16·53
H	5·64	5·52
V_2O_5	62·34	62·81

(4.) *Trimethylamine Metavanadate.*—All attempts to prepare such a metavanadate proved unavailing, an admixture of the acid vanadate was always present, and this gave a yellow product which could not be washed out, and if recrystallisation is resorted to, more of the metavanadate is transformed into the acid vanadate during the process.

(5.) *Tetrethylammonium Metavanadate*, $N(C_2H_5)_4.VO_3$.—This salt was prepared by the addition of vanadic acid to a 10 per cent. solution of tetrethylammonium hydroxide; the corresponding salt from tetramethylammonium hydroxide did not crystallise in a definite manner; it formed a crust, however, on the surface of the liquid, and after repeatedly washing it with alcohol and ether, it was ultimately obtained in a large clear tabular crystal weighing several grams. The mean results of three concordant analyses gave :—

	Found.	Calculated.
C	41·94	41·89
H	8·48	8·72
V_2O_5	39·49	39·79

The Acid Vanadates.—These separate out from the yellow solutions in splendid red hydrated crystals belonging to the monosymmetric

system, and closely resembling potassium dichromate in appearance. The crystals give up a portion of their water of crystallisation when exposed to air, and the brilliancy of the surface is thereby impaired.

No attempt was made to prepare more complicated acid vanadates, as the immediate object in view was the preparation of a series of vanadates of definite composition. By special treatment of the mother-liquor, other vanadates would no doubt be obtained, and in some instances were observed; it is not proposed to discuss these. The following are the results of the analyses of the vanadates more fully examined.

(6.) *Two-thirds Methylamine Vanadate*, $2[N(CH_3)H_3]_2O,3V_2O_5,3H_2O$,

0·394 gram gave 0·0885 gram of CO_2 and 0·131 gram of H_2O*.
0·480 „ 0·034 „ H_2O as water of crystallisation.
0·4605 „ 0·334 „ V_2O_5.

	Found.	Calculated.
C	6·12	6·30
H	2·95	3·15
V_2O_5.....	72·53	71·88
H_2O	7·08	7·09

(7.) *Two-thirds Dimethylamine Vanadate*,

$$2[N(CH_3)_2H_2]_2O,3V_2O_5,4H_2O,$$

0·3535 gram gave 0·145 gram of CO_2 and 0·1445 gram of H_2O.
0·595 „ 0·0525 „ H_2O, as water of crystallisation.
0·374 „ 0·245 „ V_2O_5.

	Found.	Calculated.
C	11·19	11·59
H	3·55	3·83
V_2O_5.....	65·51	65·52
H_2O	8·83	8·62

(8.) *Three-fifths Trimethylamine Vanadate*,

$$3[N(CH_3)_3H]_2O,5V_2O_5,7H_2O,$$

0·3605 gram gave 0·198 gram of CO_2 and 0·165 gram of H_2O.
0·2822 „ 0·0257 „ H_2O as water of crystallisation.
0·5165 „ 0·333 „ V_2O_5.

	Found.	Calculated.
C	14·98	14·93
H	4·07	4·09
V_2O_5.....	64·47	63·07
H_2O	9·10	8·71

* In this and the three following cases, the water of crystallisation is here included.

(9.) *Two-thirds Ethylamine Vanadate*, $2[N(C_2H_5)H_3]_2O,3V_2O_5,3H_2O$,

0·359 gram gave 0·151 gram of CO_2 and 0·143 gram of H_2O.
0·348 „ 0·025 „ H_2O as water of crystallisation.
0·345 „ 0·233 „ V_2O_5.

	Found.	Calculated.
C	11·48	11·74
H	3·63	3·91
V_2O_5.....	67·53	66·96
H_2O	7·18	6·60

The water of crystallisation was determined by heating the salt at 100° until the weight was constant. As there was some likelihood of decomposition occurring at this temperature, an experiment was made in the following way to determine whether this actually took place. Some of the powdered salt was heated in a current of perfectly dry air at 100° until constant; the air was afterwards passed over soda-lime as being a suitable absorbent in this case. The loss of weight of 1·2845 grams of vanadate was 0·1265 gram, the gain in weight of the soda-lime being 0·1255 gram; so that no appreciable amount of the ammonia base is set free by heating at 100°. As a further check the air was shown to be free from the alkaline base, by heating the salt in dry air and using a standard solution of acid in the place of the soda-lime.

Considered alongside the vanadates of the alkali metals, we notice that the orthovanadates of the amines present the same difficulties in the way of preparation that the corresponding potassium salts do, whereas the sodium orthovanadate is readily crystallised. The metavanadates of the amines are much more soluble than the ammonium metavanadate with which, however, they agree in general characters and in their qualitative reactions. The derivatives of the primary amine crystallise well, but the further introduction of alcohol radicals decreases the stability of this series of salts, as is seen by the fact that the metavanadate of the tertiary amine could not be obtained pure.

The salts containing the ethyl radical seem to be at least as stable as corresponding ones containing the methyl radical. The optical characters of the red vanadates show that they belong to the monosymmetric system, and such measurements as have been made agree with this. A complete set of measurements, however, has not yet been made, as the precision of the work is much interfered with by a slight dulness which comes over the surface of the crystal on prolonged exposure.

LVI.—*The Origin of Calcium Thiosulphate: an Emendatory Note to a Paper on the Calcium Hydrosulphides.*

By Edward Divers.

Of the paper by T. Shimidzu, M.E., and myself, on the calcium hydrosulphides, which appeared in the *Journal of the Chemical Society* (Trans., 1884, p. 270), the concluding section is taken up with a consideration of the formation of calcium thiosulphate from the hydrosulphides. Upon the basis of experimental results recorded in it, we concluded that the process of oxidation takes place principally in hydrogen sulphide liberated by hydrolysis. This being the case, we attributed the formation of the pentasulphide to the action of the sulphur on calcium hydrosulphide, and that of the thiosulphate to some action of oxidised or oxidising sulphur on calcium hydroxyhydrosulphide, giving an equation for this, which seemed an improvement on previously published ones, but which was admittedly not so explicit concerning what happened as could have been wished.

The fact that lime and sulphur when boiled together in water yield pentasulphide and thiosulphate was not left out of sight in the paper, and was even experimentally examined; in particular we recorded that in the cold we had not observed any appreciable action between lime and sulphur in water. But this section on thiosulphate was in some sort an appendix to the main subject of the paper, and only at the time of preparing and putting together our description of experiments, had we given any thought to the nature of the formation of thiosulphate from the hydrosulphide, and we wrote under the influence of traditional teaching as to the action of the atmosphere.

Further consideration has led me to recognise that the usual assumption that the thiosulphate results from the atmospheric oxidation of sulphur, either combined or free, is much more difficult to accept than to assume that it is formed by the action of sulphur on calcium hydroxide, and in no other way. As our paper furnishes the grounds on which this recognition is based, and only contains half a dozen lines that I would now cancel, I may be brief in stating my present theory of the changes which occur in the conversion of calcium hydrosulphide to thiosulphate.

First, *the calcium hydrosulphides by hydrolysis become calcium hydroxide and hydrogen sulphide.* The extent to which this second degree of hydration of calcium sulphide proceeds is limited by the accumulation of hydrogen sulphide, but when this is removed as fast as it is formed, its production continues to the end. Secondly, *the hydrogen sulphide*

is oxidised by the air, and not the calcium salts. The well-known oxidation of hydrogen sulphide is slow, but still quick enough to correspond with the rate at which the apparent oxidation of the hydrosulphides proceeds. Proof of this has already been given in the paper on the hydrosulphides; and since air always meets these substances in presence of hydrogen sulphide derived from them, there is no evidence that they oxidise directly at all. Thirdly, *of the hydrogen sulphide only the hydrogen oxidises:* (1), the action of sulphur on lime being a sufficient explanation of the production of both pentasulphide and thiosulphate; (2), the oxidation of sulphur being hardly a justifiable assumption; (3), the reaction of oxidised sulphur to form thiosulphate under the circumstances being an improbable one; and (4), the recognition of the formation of unoxidised sulphur being after all a necessity in order to explain the production of pentasulphide.

Fourthly, *sulphur and calcium hydroxide react,* as they do when boiled together, *to form calcium pentasulphide and thiosulphate.* Here only is any assumption made. Common sulphur and lime have scarcely any action on each other in cold water; but the assumption here made is that they do react freely *when the sulphur is but just formed and in intimate contact with the lime.* In support of this assumption, it may be pointed out that pentasulphide and thiosulphate are not formed, one without the other, in the oxidation of calcium hydrosulphides, and that at first the pentasulphide may be largely in excess of the thiosulphate although it is not known to have been in such excess as the following equation requires:—

$$3CaO_2H_2 + 12S = CaS_2O_3 + 2CaS_5H.OH + H_2O.$$

But then this fact is in accordance with what is known of the transformation of the pentasulphide by (indirect) oxidation into the thiosulphate; for if only a seventh of the pentasulphide in the above proportion were to become thiosulphate, the altered proportion would be such as has been several times found by Kraushaar in his experiments on the oxidation of soda-waste.

Lastly, *the change of pentasulphide into thiosulphate is the same in nature as that of a calcium hydrosulphide into it,* with the exception that additional lime is needed, in order that no sulphur may be deposited. *There is no direct oxidation of the pentasulphide,* but only (1) the proved hydrolysis of the pentasulphide into sulphur, hydrogen sulphide, and lime; (2), the atmospheric oxidation of the hydrogen of the hydrogen sulphide; (3), the reaction of the sulphur with lime to form thiosulphate and again some pentasulphide, this then to undergo a repetition of these changes; and (4) so forth to the end of the conversion. It is not my intention here to ignore that calcium penta-

sulphide may be formed from hydrosulphide and sulphur, as it is described to be in the paper on calcium hydrosulphides; but this source of pentasulphide is, I think, quite a subordinate one.

The adoption of the theory I have here enunciated, reduces by one the methods in which thiosulphate appears to be formed. Besides the method of forming it from sulphur and lime, there are two others—that in which it is formed by the action of sulphur dioxide on a hydrosulphide, and that in which it is formed by the action of sulphur on a sulphite. I do not here count the oxidation of a hydrosulphide by copper oxide, because that appears to be only the substitution of this oxide for the air as a source of oxygen. The question now presents itself, whether the three methods are not essentially one.

When sulphurous acid reacts with calcium hydrosulphide, the change cannot be represented very simply, as we know, and the most satisfactory manner of doing so appears to be that calcium sulphite is formed, that hydrogen sulphide and sulphurous acid form sulphur, and that *this sulphur combines with the calcium sulphite.*

Coming next to the joint formation of pentasulphide and thiosulphate by the reaction between sulphur and lime, we must, in dissecting this reaction, recognise that two atoms of calcium are removed from oxygen and combined with sulphur, and that the two oxygens left free unite with one of sulphur, thus—

$$2CaO_2H_2 + 11S = 2CaS_5H.OH + SO_2.$$

In other words, that sulphur, like chlorine, in contact with lime, divides itself between the metal and the oxygen. This, I say, seems certain; and then this will be followed by, first, the formation of calcium sulphite from sulphurous acid and lime, and secondly, *the union of this sulphite with sulphur* to form thiosulphate. If it seems at all strained to represent some of the sulphur as oxidising and combining with lime and *then* taking up more sulphur, it should be remembered that half the sulphur of thiosulphate is assuredly unoxidised and feebly combined.

Two of the methods are thus apparently only cases of the third one, which consists in *the union of sulphur with calcium sulphite;* and there is essentially but one method of forming thiosulphate (the union of sulphurous acid with a hydrosulphide being in fact only apparent).

LVII.—*Magnesium Hydrosulphide Solution, and its Use in Chemico-legal Cases as a Source of Hydrogen Sulphide.*

By Edward Divers, M.D., and Tetsukichi Shimidzu, M.E.,
Imperial Japanese College of Engineering.

The introduction of magnesium hydrosulphide into the arts, as a means of recovery of the sulphur of soda-waste in the form of hydrogen sulphide, led us, in the summer of 1882, to employ it as a source of hydrogen sulphide in the laboratory. Artificially prepared *iron sulphide* yields hydrogen as well as hydrogen sulphide, and we wanted for our experiments hydrogen sulphide in the undiluted state. *Antimony sulphide* and boiling solution of hydrochloric acid form a very unsatisfactory source of the gas when this is wanted in a long-continued, steady stream. *Blende* from its usual admixed minerals is still more unsuitable.

We had tried *pyrrhotite*, probably never before used for this purpose, and found it work satisfactorily in place of artificial iron sulphide, especially with hydrochloric acid slightly warm and not too dilute. But all pyrrhotite that we could get from different parts of this country yielded at least small quantities of carbon dioxide from the calcite it contained, and the pyrrhotite in powder was too sensitive to dilute acid to allow of the calcite being dissolved out from it. Now there is, so far as we know, no means* of removing carbon dioxide from hydrogen sulphide, since carbonates, even of the alkaline earths, are decomposed by hydrogen sulphide. It is not always, however, of consequence, even if the hydrogen sulphide is mixed with a little carbon dioxide, and we may recommend pyrrhotite as one source of arsenic-free hydrogen sulphide.

The well-known and important observation of J. and R. Otto that artificial iron sulphide when treated with an acid yields hydrogen arsenide along with the hydrogen sulphide, if either acid or iron sulphide contains arsenic, gives a special value to other sources of the gas not liable to this defect. From the experiments of R. Otto, it appears to be the free iron in the artificial iron sulphide which in presence of

* With one exception, that is. The mixed gases may be separated by passing them through a *hot* solution of calcium or magnesium hydrosulphide, which will retain most, if not all, of the carbon dioxide. This method is useless for analytical purposes, because the hydrosulphides give off much additional hydrogen sulphide; and it is almost useless for getting pure hydrogen sulphide, because these hot washing-solutions are themselves a sufficient source of the gas without the aid of the pyrrhotite.

arsenic sulphide and acids generates the hydrogen arsenide. It was, therefore, to be expected that pyrrhotite would yield hydrogen sulphide free from arsenic even if the acid used contained it, and in some experiments we made under these conditions we failed to find the least trace of arsenic volatilised. However, magnesium hydrosulphide solution is not only a more convenient material than pyrrhotite from which to prepare hydrogen sulphide free from arsenic, but it is more unobjectionable, for we need not insist on the importance of having our reagents above suspicion, and accordingly of not going to possibly arseniferous materials, mineral or acid, for pure hydrogen sulphide. It may, perhaps, be the case, too, that pyrrhotite obtained in other countries will not prove such a convenient source as Japanese pyrrhotite. This pyrrhotite is, indeed, remarkable in containing no nickel, and only an infinitesimal amount of cobalt, and may be softer and more sensitive to acids than other pyrrhotites.

R. Otto recommends the use of calcium or barium sulphide with hydrochloric acid as a means of obtaining hydrogen sulphide free from arsenic; from such a source, however, it will of course hardly ever be free from carbon dioxide. He recommends the use of hydrochloric acid free from arsenic, although, as he points out, no hydrogen arsenide can in any case be formed. The sulphide is used in the solid state, and is so sensitive to the action of acids that, in order to get a sufficiently steady stream of gas, the acid must be supplied from a dropping-funnel. Magnesium hydrosulphide solution, however, is easier to procure and easier to use than the above sulphides, and moreover requires no addition of acid. In our opinion, it is very superior to them as a source of hydrogen sulphide.

Preparation of Magnesium Hydrosulphide Solution.

Hydrogen sulphide obtained from ordinary iron sulphide, and either sulphuric or hydrochloric acid, is passed into a large flask half or two-thirds full of water holding magnesia suspended. If the magnesia happens to be carbonated, as is usual in its commercial forms, this matters little, although freshly calcined magnesia is preferable, as being more easily dissolved. The proportion of magnesia to water must not be too great, one part of commercial impure oxide in ten parts of water being near the limit. An excess of magnesia seems to prevent the formation of such a concentrated solution as can be obtained when the proper quantity is not exceeded. The magnesia slowly dissolves in the stream of gas, much of which, it is hardly necessary to state, passes away unabsorbed. Where, therefore, as in most laboratories, hydrogen sulphide gas is in nearly constant use, the flask of magnesia may conveniently be interposed between the

generator and such solutions as require treatment with the gas. When the solution has been prepared, the flask can be corked to exclude air, or at once used if wanted. It may be preserved unchanged for any time by sealing over the cork with wax or paraffin. Magnesium hydrosulphide solution may also be prepared, of course, as in the magnesia method of sulphur recovery by the reaction between calcium sulphide and magnesium chloride; but for laboratory purposes such a method presents no advantages.

Some Properties of Magnesium Hydrosulphide Solution.

A solution found by us to contain 4·35 per cent. of magnesium, equal to 16·31 per cent. of magnesium hydrosulphide, MgS_2H_2, may serve to represent what will usually be obtained by proceeding as above directed. Its sp. gr. was 1·118 at 12°. Such a solution is capable of yielding 12 per cent. of hydrogen sulphide by weight, and readily in practice, 10 per cent., let us say, the amount varying according to circumstances.

The solution, when the impurities of the magnesia have settled down, is nearly colourless, its slight colour being due to polysulphide formed by the action of ferric oxide in the magnesia or of air. Exposed to the air, or heated to about 60° in a flask with delivery-tube, it gives off hydrogen sulphide. But exposure to air also results in oxidation of the hydrosulphide to polysulphide and thiosulphate. However, in a solution left at rest, oxidation is much impeded by the formation of a firm, colourless, transparent, amorphous film on the surface of the liquid, consisting apparently of magnesium hydroxide, but possibly of hydroxyhydrosulphide, MgSH.OH. The solution does not readily, if at all, absorb carbon dioxide from the atmosphere in the early stage of its decomposition.

With regard to the effect of heat, already mentioned, a temperature of 60—65° gives a steady evolution of hydrogen sulphide for some time, and this can be maintained for a considerable time longer by raising the temperature to 90—100°. As hydrogen sulphide escapes, magnesium hydroxide separates out in the solid state. These facts are now well known in connection with the process of sulphur-recovery. The poly- (penta- ?) sulphide that may be in solution is only very slightly decomposed even at a boiling heat, but in so far as it is, it yields hydrogen sulphide, solid sulphur, and magnesia. The yellow polysulphide is however readily decomposed by hydrogen sulphide, the products being magnesium hydrosulphide and sulphur. It is hardly necessary to add, that magnesium hydrosulphide will decompose with an acid, and may thus be made if desired to yield its hydrogen sulphide like calcium, barium, iron, and other sulphides.

Employment of the Solution as a Source of Hydrogen Sulphide free from Arsenic.

The mode of employing it will be obvious. The flask containing it, provided with a simple delivery-tube, and without washing-bottle, is to be heated, best on a water-bath, to the extent necessary to secure a steady stream of gas. It may often be an advantage to make the following arrangement:—Put the solution to be treated with the gas into a flask or bottle fitted with cork and gas-entry tube, and connect its tube with the delivery-tube of the generator. Keeping the test-flask slightly open, warm the generator until the air is entirely expelled from both flasks, and then close the test-flask tight. The generator being kept warm, the hydrogen sulphide may be sent over into the solution under treatment without waste and without access of air. The level of the liquid in the tube of the test-flask will guide the operator in heating the generator. The gas being unmixed with hydrogen will be absorbed much faster than it is commonly seen to be, and with such an arrangement some little attention is necessary or the solution may be carried over into the generator through the reabsorption of the gas by the magnesia, should this from any cause be allowed to cool a little.

The evolution of hydrogen sulphide from the magnesium salt by heat has advantages over that by the addition of acids to alkaline-earth and other sulphides; firstly, in being steady and under perfect control, and, secondly, in yielding the gas free from any other, active or inactive, except a little water-vapour, free from the spray which effervescence by acids causes, and in no need therefore of any washing.

When the magnesium solution has been used until nearly exhausted, it has only to be placed again, when cold, in a current of ordinary hydrogen sulphide to be restored nearly or fully to its first strength as a source of this gas. Magnesium hydroxide, carbonate, and polysulphide will all thus be reconverted to hydrosulphide, and only the little thiosulphate remain unchanged. After using many times, or after much accidental exposure to the air, the contents can be replaced with fresh magnesia and water with but little cost or trouble.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY,

SESSION 1883–84.

November 1st, 1883.

Dr. W. H. Perkin, F.R.S., President, in the Chair.

The following papers were read:—

"On the Formation of Hydroxylamine from Nitric Acid;" by E. Divers.

"On the Chemistry of Lacquer" (Part I): by H. Yoshida.

"On some Compounds of Phenols with Amido-bases:" by G. Dyson.

"On the alleged Decomposition of Phosphorous Anhydride by Sunlight:" by R. Cowper and V. B. Lewes.

November 15th, 1883.

Dr. W. H. Perkin, F.R.S., President, in the Chair.

The following papers were read:—

"On the Estimation of Starch:" by C. O'Sullivan.

"On the Illuminating Power of Ethylene when burned with Non-luminous Combustible Gases:" by P. F. Frankland.

"On the Products of Decomposition of Aqueous Solutions of Ammonium Nitrite:" by G. S. Johnson.

"On the Estimation of Iron by Potassium Bichromate:" by E. B. Schmidt.

December 6th, 1883.

Dr. W. H. Perkin, President, in the Chair.

Messrs. F. A. Blair, T. J. Baer, C. J. Baker, L. Briant, R. G. Durant, Kamchandra Datta, L. L. Garbutt, A. E. Harris, T. Hart, W. Irwin, S. Johnson, R. Jackson, H. C. Lee, W. H. Martin, C. E. Potter, B. M. H. Rogers, C. W. Stephens, P. H. Wright, H. A. Wetzell, W. G. Whettam, were elected Fellows of the Society.

The following papers were read:—

"On the Constitution of the Fulminates:" by E. Divers and M. Kawakita.

"Theory of the Constitution of the Fulminates:" by E. Divers.

"On Liebig's Production of Fulminating Silver without the use of Nitric Acid:" by E. Divers and M. Kawakita.

"Note on the Constitution of the Fulminates:" by H. E. Armstrong.

"Experimental Investigations on the Value of Iron Sulphate as a Manure for certain Crops:" by A. B. Griffiths.

December 20th, 1883.

Dr. W. H. Perkin, President, in the Chair.

Messrs. W. P. Bloxam, A. Cobb, G. C. Chambers, A. E. Ekins, F. P. Haviland, F. Keeling, W. H. R. Kerry, J. J. Pilley, M. Percy, J. Phillips, A. W. Rogers, W. J. Saint, G. Smith, A. Smithells, were elected Fellows of the Society.

The following papers were read:—

"Researches on the Gums of the Arabin Group (Part I): Arabic Acid, its Composition and Products of Decomposition:" by C. O'Sullivan.

"On the Decomposition of Ammonia by Heat:" by W. Ramsay and Sidney Young.

"On the Halogen Compounds of Selenium:" by G. P. Evans and W. Ramsay.

"On the Preparation of pure Chlorophyll Pigment:" by C. Tchirsch.

January 17th, 1884.

Dr. Perkin, F.R.S., President, in the Chair.

Messrs. B. H. Brough, G. Daubeney, C. C. Hutchinson, W. S. Kilpatrick, E. Matthey, H. Peile, J. W. Pallister, R. Romanis, W. O. Senior, J. A. Voelcker, were elected Fellows of the Society.

The following papers were read:—

"On Camphoric Peroxide and Camphorate of Barium:" by C. T. Kingzett.

"Supplementary Note on Liebig's Production of Fulminating Silver without the use of Nitric Acid:" by E. Divers and M. Kawakita.

"On the Decomposition of Silver Fulminate:" by E. Divers and M. Kawakita.

"On Hyponitrites:" by E. Divers and Tamemasa Haga.

February 7th, 1884.

Dr. Perkin, F.R.S., President, in the Chair.

The following papers were read:—

"On the Expansion of Liquids:" by D. Mendelejeff, translated from the Russian by B. Brauner.

"Researches on Secondary and Tertiary Azo-compounds." No. II: by R. Meldola.

"On the Nitrogenous Matters in Grass and Ensilage from Grass:" by E. Kinch.

"On the Influence of the Temperature of Distillation on the Composition of Coal-gas:" by L. T. Wright.

February 21st, 1884.

Dr. Perkin, F.R.S., President, in the Chair.

Messrs. L. Archbutt, J. H. Burland, D. Bain, W. H. Barr, R. A. Busch, P. S. Chantrell, A. F. Damon, H. C. Draper, T. R. Duggan, V. Edwards, W. T. H. Elsley, G. W. Gibson, F. W. Harris, T. Hilditch, R. E. Moyle, P. Morton, W. J. Orsman, F. R. Power, A. E. Simpson, C. W. Sutton, H. G. Shaw, E. F. Smith, F. W. Tompson, A. Tarn, and E. W. Voelcker, were elected Fellows of the Society.

The following papers were read:—

"On the Composition of the Ash of Wheat-grain and Straw grown

at Rothamsted in Different Seasons and with Different Manures:" by Sir J. P. Lawes and Dr. J. H. Gilbert.

"On the Analysis of Shotley Bridge Spa-water:" by H. Peile.

March 6th, 1884.

Dr. Perkin, F.R.S., President, in the Chair.

The following papers were read:—

"Studies on Sulphonic Acids. No. I. On the Hydrolysis of Sulphonic Acids, and on the Recovery of Benzenes from their Sulphonic Acids:" by H. E. Armstrong and A. K. Miller.

"On a Relation between the Critical Temperatures of Bodies and their Thermal Expansions as Liquids:" by T. E. Thorpe and A. W. Rücker.

"Remarks on the Densities of Members of Homologous Series:" by W. H. Perkin.

"Note on some Experiments made at the Munster Agricultural School to determine the Value of Ensilage as a Milk- and Butter-producing Food:" by T. Farrington.

"Note on the Behaviour (1) of the Nitrogen of Coal during Distillation, and (2) a Comparison of the Amounts of Nitrogen left in Cokes of Various Origins:" by Watson Smith.

"On a Hitherto Unnoticed Constituent of Tobacco:" by T. J. Savery.

March 20th, 1884.

Dr. Perkin, F.R.S., President, in the Chair.

Messrs. F. W. Brown, H. Cave, F. W. Fleming, E. E. Graves, A. E. Lewis, J. E. London, G. A. Parkinson, S. Smith, G. Tunbridge, and T. W. Walton were elected Fellows of the Society.

The following papers were read:—

"Note on the Preparation of Marsh-gas:" by Dr. J. H. Gladstone.

"On the Action of Dibrom-α-naphthol upon Amines:" by R. Meldola.

"Note on the Existence of Salicylic Acid in the Cultivated Varieties of Pansy and in the Violaceæ generally:" by A. B. Griffiths.

March 31st, 1884. (Anniversary Meeting.) See page 209.

April 3rd, 1884.

Dr. Perkin, F.R.S., President, in the Chair.

The following papers were read:—

"On the Influence of Certain Phosphates upon Vinous Fermentation:" by A. G. Salomon and W. de Vere Mathews.

"On the Occurrence of Rhabdophane in the United States:" by W. N. Hartley.

April 17th, 1884.

Dr. Perkin, F.R.S., President, in the Chair.

Messrs. J. P. Battershall, W. D. Borland, J. C. Bose, W. D. Crumbie, A. F. Dimmock, H. G. Greenish, W. J. Gray, J. Gaskell, J. W. Pratt, A. G. Perkin, W. H. Perkin, jun., and G. H. Wainwright, were elected Fellows of the Society.

The following papers were read:—

"On the Influence of Incombustible Diluents on the Illuminating Power of Ethylene:" by P. F. Frankland.

"On Trichloropyrogallol:" by C. S. Webster.

"The Synthesis of Galena by means of Thiocarbamide:" by J. Emerson Reynolds.

"On the Analysis of Woodall Spa:" by W. T. Wright.

"On the Critical Temperature of Heptane:" by T. E. Thorpe and A. W. Rücker.

May 1st, 1884.

Dr. Perkin, F.R.S., President, in the Chair.

The following papers were read:—

"On Benzoylacetic Acid and some of its Derivatives." Part I: by W. H. Perkin, jun.

"On the Composition of Coal- and Cannel-gas in Relation to their Illuminating Power:" by P. F. Frankland.

"On Selenium Sulphoxide. (2) On the Reaction between Hydrogen Chloride and Selenium Sulphoxide, and (3) on Selenium Seleniochloride:" by E. Divers and M. Shimosé.

"On Fluorene." Part II: by W. R. E. Hodgkinson.
"On a New Form of Pyrometer:" by T. Carnelley and T. Barton.

May 15th, 1884.

Dr. Perkin, F.R.S., President, in the Chair.

The following papers were read:—

"On Refraction Equivalents of Organic Compounds:" by J. H. Gladstone.
"On the Estimation of Silicon in Iron and Steel:" by T. Turner.
"Note on the Melting Points and their Relation to the Solubility of Hydrated Salts:" by W. A. Tilden.
"Minor Researches on the Action of Ferrous Sulphate on Plant-life:" by A. B. Griffiths.
"Note on Ferric Sulphocyanate:" by A. J. Shilton.

June 5th, 1884.

Dr. W. H. Perkin, F.R.S., President, in the Chair.

The following papers were read:—

"On β-Naphthaquinone:" by C. E. Groves.
"On a Bye-product of the Manufacture of Aurin (Part II):" by A. Staub and Watson Smith.
"On Calcium Hydrosulphides:" by E. Divers and T. Shimidzu.

June 19th, 1884.

Dr. W. H. Perkin, F.R.S., President, in the Chair.

Messrs. W. Alabaster, H. B. Baker, W. T. Burgess, E. G. B. Barlow, R. D. Courtney, E. J. Caley, M. H. Foye, W. F. Tremensdorff, W. F. Grace, J. Hargreaves, Baron F. von Meuller, E. L. C. Muspratt, F. Nettlefold, A. G. Page, J. Parr, E. H. Rogers, R. S. Stephens, T. Stormouth, R. C. Tressider, A. J. Watts, and J. T. Wells, were elected Fellows of the Society.

The following papers were read:—

"On the Magnetic Rotary Polarisation of Chemical Compounds in

Relation to their Composition; with Observations on the Preparation and Densities of the Bodies Examined:" by W. H. Perkin, F.R.S.

"On the Effect of High Temperatures on Petroleum Hydrocarbons:" by H. E. Armstrong and A. K. Miller.

"On the Decomposition of Terpenes by Heat:" by W. A. Tilden.

"Note on the General Law which governs the Dilatation of Liquids:" by P. de Heen.

"On the Melting Points of Certain Inorganic Substances:" by T. Carnelley and L. T. O'Shea.

"On Nitrification (Part II):" by Robert Warington.

Donations to the Library, 1884:—

"Reports of the British Association for the Advancement of Science, 1833–1837:" from the Association.

"The Chemistry of the Secondary Batteries of Planté and Faure:" by J. H. Gladstone and A. Tribe: from the Authors.

"Annual Report of the Board of Regents of the Smithsonian Institution for 1881:" from the Institution.

"Transactions of the Brighton Health Congress," 1881: from J. E. Mayall, Esq.

"Proceedings of the Philosophical Society of Glasgow," 1882–1883, Vol. xiv: from the Society.

"Agricultural Chemical Analysis:" by P. F. Frankland: from the Author.

"Potable Water:" by Chas. Ekin: from the Author.

"The Chemical Effect of the Spectrum:" by J. M. Eder: Translated by Capt. Abney: from the Translator.

"Steel and Iron:" by W. H. Greenwood: from the Author.

"The Periodic Law:" by J. R. Newlands: from the Author.

"The Electricians' Directory, with Handbook for 1884:" from the Editor.

"Journal of the American Chemical Society." Vol. vi, Nos. 1 and 2, January, February, 1884: from the Society.

"The Unity of Matter:" by G. T. Carruthers: from the Author.

"Organic Chemistry:" by P. Alexejeff: from the Author.

"A Treatise on Chemistry:" by Professors Roscoe and Schorlemmer; Vol. iii, Organic Chemistry, Part II: from the Authors.

"Pharmaceutical Journal:" Vols. x, xi, xii, xiii, parts of Vol. v: from the Society.

"The Non-Bacillar Nature of Abrus-Poison:" by C. J. H. Warden and L. A. Waddell: from the Authors.

"Nicolas Leblanc, sa Vie, ses Travaux, et l'Histoire de la Soude Artificielle:" from Aug. Anastasi.

"Action of Cyanogen on Metatoluidine:" by J. A. Bladin.

"Mononitronaphthalene α-Disulphochloride and New Naphthalene-Derivatives obtained from it:" by J. E. Alèn.

"Dinitronaphthalene α-Disulphochloride and New Naphthalene-Derivatives obtained from it:" by J. E. Alèn:
from the Royal Swedish Academy of Sciences.

"Verhandlungen der Naturforschenden Gesellschaft in Basel." 7te Theil, 2te Heft, 1884.

"Die Basler Mathematiker, Daniel Bernoulli und Leonhard Euler; hundert Jahre nach ihrem Tode gefeiert von der Naturforschenden Gesellschaft," Basel, 1884: from the Society.

"First, Second, and Third Reports of the State Board of Health, New York:" from the Board.

"Analisi Chimica delle Acque potabili della Città di Roma eseguita por vicarica del Municipio:" dal Prof. Mauro e dai Dottori R. Nasini e A. Piccini, Roma, 1884: from the Authors.

"Sketch of the Life and Scientific Work of Dr. Johnson Lawrence Smith:" by B. Silliman: from the Author.

"Introduction to the Study of the Scientific Principles of Agriculture:" by J. H. Gilbert: from the Author.

"Transactions of the Royal Irish Academy." Vol. xxviii, Nos. 14, 15, 16.

"Proceedings of the Royal Irish Academy." Series II, Vol. iv, Nos. 1 and 2; and Vol. ii, No. 5.

"Qualitative Chemical Analysis," 3rd Edition: by T. E. Thorpe.

"Quantitative Chemical Analysis," 5th Edition: by T. E. Thorpe:
from the Publishers.

"Inorganic Chemistry:" by E. Frankland and F. R. Japp:
from the Authors.

"Principles of the Manufacture of Iron and Steel:" by I. Lowthian Bell: from the Author.

"Mineral Resources of the United States:" by A. Williams, Junr.

"Report of the United States Geological Survey:"
from the Director.

"Transactions of the Sanitary Institute of Great Britain:"
from the Society.

"Quarterly Journal of the Chemical Society." Vol. v, Nos. 3 and 4; and Vol. viii, No. 1: from Prof. Liversidge.

"Final Report of the South Australian Institute:"
from the Institute.

"Handbuch der Organischen Chemie:" von F. Beilstein, 2te Auflage, Hefte 1 and 2: from the Author.

"Descriptive Catalogue of the Exhibits of the Japanese Home Department at the Health Exhibition:"

from the Japanese Commission.

"Elements of Agricultural Chemistry:" by Sir Humphry Davy, London, 1813. Presented by Mr. C. W. Watts.

"Proceedings of the Birmingham Philosophical Society:"

from the Society.

The following were presented by Professor Chandler:—

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„	10	„	„	"reduction"	„ "action."

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21	20	„ „	„	H.OC	„ HOC.
24	10	„ „	„	Br_2CN	„ $NCBr_2$.
24	10	„ „	„	Br_2CNO	„ $(O_2N)CBr_3$.
24	16	„ „	„		„
25	8	from top,	„	(HO.N)C.H.NO)	*read* (HO.N)C.CH.NO.
26	bottom line.		The formula for fulminic acid should be		
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288	17	„ top,	„	"form of oxidation here assumed to take,"	*read* "assumption that such an oxidation takes."
408	3	„ „	„	"P. D. Hein,"	*read* "P. De Heen."

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